

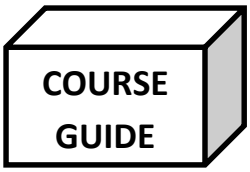
NATIONAL OPEN UNIVERSITY OF NIGERIA

FACULTY OF SCIENCE

DEPARTMENT OF PURE AND APPLIED SCIENCES

COURSE CODE: 409

COURSE TITLE: ELECTROCHEMISTRY



CHM 409

ELECTROCHEMISTRY

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INTRODUCTIONS

Electrochemistry is a science that study interactions of chemical and electrical energies. This includes the study of chemical changes caused by the passage of an electric current across a medium, as well as the production of electric energy by chemical reactions. Electrochemistry also embraces the study of electrolyte solutions and the chemical equilibrium that occur in them.

Many chemical reactions require the input of energy and can be carried out in an electrochemical cell connected to an external power supply. These reactions can provide information about the nature and properties of the chemical species contained in the cells, and can also be used to synthesize new chemicals. The production of sodium, chlorine and aluminium and the electroplating and electrowinning of metals are examples of industrial electrochemical processes. Other examples are cathodic and anodic protection of metals against corrosion.

Electrochemical cells that produce electric energy from chemical energy are the basis of primary cells, secondary (storage) batteries and fuel cells. Other electrical phenomena of interest in chemical systems include the behaviour of ionic solutions and the conduction of current through these solutions, the separation of ions by an electric field (electrophoresis), the corrosion and inertness of metals, electrical effects in biological systems (bio-electrochemistry), and the effect of light on electrochemical cells photoelectrochemistry).

In electrochemistry, two broad areas are involved. These are electrodics and Ionics. Ionics deals with ions in solution and conductivity while electrodics deals with the production of electricity by electrochemical reactions and the production of an electrochemical reactions by an applied electromotive force. Basic features in Ionics include conductivity, migration of ions, etc.

Conductivity in electrolyte is due to mobility of ions. When a salt is dissolved in water, the energy required, is provided by hydration. The extent of hydration depends on the size and charge of the ion. A small highly charged ion such as K^+ will be easily hydrated than Al^{3+}, which has higher size and charge. Hydrated ions of opposite charge show little tendency to attract ion in aqueous solution because the high permittivity (ε) of water reduces the force (i.e, F) between charges, q_1 and q_2. For two oppositely charge ions with magnitudes, q_1 and q_2, the columbic interaction between them is given as,

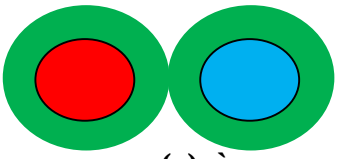
$$F = \frac{q_1 q_2}{4\pi l^2 \varepsilon} \qquad 1.1$$

where l is the distant of separation between the charges. ε is the dielectric constant of the solvent. ε= 78.54 for water at 298 K.

Another factor that may affects the conductivity of an electrolyte solution is the association of water molecule with ions (i.e. formation of hydration sheath). This is capable of inhibiting ionic association and can hinder conductivity. For example, at high concentration, Mg^{2+} and SO_4^{2-} associate according to the following equation:

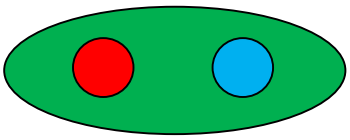
$$Mg^{2+} + SO_4^{2-} = Mg^{2+}SO_4^{2-} \qquad 1.2$$

This association can hinder the conductivity of the electrolyte because ions pairs do not conduct electricity. Ion pair can be classified as fully solvated, solvent-shared/solvent-separated and contact ion pair. In the Figure below, the solvent is coloured green while the cation and the anion are coloured red and light blue respectively. The diagram represents fully solvated ion pair because both ions (cation and anion) have complete solvation sphere



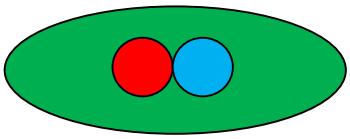
(a)

However, when there are one solvent molecules between the cation and the anion, the ion pair is termed solvent-shared or solvent separated. This is shown in the diagram below (b)



(b)

Finally, when the ions are in contact with each other, the ion pair is called contact ion pair (c)



(c)

Different ion pairs affect conductivity of electrolyte differently. Generally, the formation of ion pair in an electrolyte will lowers its conductivity.

Electrodics

Electrodics is concerned with electrode and reactions taking place in an electrochemical cell. Although most electrodes are metals, there are several electrodes that are non-metals. An electrode is an electronic conductor (such as metals, semiconductor, graphite or conducting polymers) that is in contact with an electrolyte. It is a system consisting of two or more electronically and ionically conducting phases, switched in series, between which charge carriers (electrons and ions) can be exchanged, one of the terminal phases being an electronic conductor (*e.g.* metal) and the other an ionic conductor (e.g. electrolyte).

In this course, we shall examine some fundamental aspects of Ionics including mass transport, polarization, interfacial interaction, polarography and associated law or theory. In view of this, let us consider some basic principles underlying the behaviour of ions in solution.

COURSE COMPETENCIES

Electrochemistry (CHM 409) is a course which addresses the behaviour of ions in solutions. CHM 409 is structured to address the theory, principles and application of what happens around electrochemical interphase. The study of electrochemical interphase is significant because most of the usefulness of electrochemistry rest on processes at the interphase. In view of this, the course introduces what is electrochemical interphase and examines type of electrochemical interphase, the electric double layer, mass transport of materials from and through the interphase, polarization at the interphase, polarography and electronics in electrochemistry. In order to bring these concepts to the understanding of the students, basic terms and topics (such as electrolysis, laws of electrochemistry, etc) are also discussed.

This course is aimed to bring the student to the knowledge of fundamental aspect, theory and laws in Ionics, an aspect of electrochemistry that deals with ions in solutions. Students will learn the concept of electric double layer, potential at zero charge, mass transport, polarization, laws of electrochemistry, mobility of ions and associated theories, derivation and applications of Nernst equation overpotential, interfacial interactions and some laws including Fick's law of diffusion, derivation of Butler Volmer, Einstein, Stoke, Wagner, Ilkovic and Levich equations.

COURSE OBJECTIVES

When you have studied this course, you should be able to

i. To introduce the students to different electrochemical cells, their operation and applications

ii. To introduce the student to electrolysis, types applications and associated laws
iii. To introduce the student to ionic mobility, associated laws and applications
iv. To introduce the concept of electric double layer and their effect on electrochemical systems
v. To explain factors that affect diffusion and the laws of diffusion
vi. To explore the significant of Stooke's law in ionic mobility and also Fick's law of diffusion.
vii. To bring the student to the understanding of the meaning of potential at zero charge and how it can be measured
viii. To explain the concept of polarization of electrodes and other electrochemical inter-phases
ix. To introduce and explain the various forms of mass transport in electrochemical systems
x. To introduce and explain the concept of polarography and their application in electrochemistry
xi. To explain the concept of electronics in electrochemistry
xii. To explore the theories and laws associated with all the listed concepts

WORKING THROUGH THIS COURSE

The course is structured into five models. Modules 1 to 3 consist of two units each while modules 4 and 5 consist of one unit each. It is necessary that for the student to study and understand the content of all the units in the respective modules.

You will be provided with the following materials:

1. Course Guide

2. Study Units

STUDY SECTIONS

This course materials is organised into three Modules. Module 1 consist of two units, module 2, two units and module 3, three units. Descriptions of each unit are as follows,

Module 1

Study unit 1: Electrochemical interphase

Study Unit 2: Electric double layer

Module 2

Study Unit 1: Polarization at interphase

Study Unit 2: Verification of Tafel equation: Butler Volmer equation

Module 3

Study Unit 1: Mass transport

Study Unit 2: Polarography

Study Unit 3: Electronics in electrochemistry

Module 1, Study Unit 1 introduces the students to electrochemical interphases and electric double layer. Unit one identified the different forms of electrochemical interphase and discuss their structure, features and possible applications. Some notable scientists that have contributed to the development of electrical interphase have been acknowledge.

In Study Unit 2 of module1, electric double layer is introduced as a process that is significant at the interphase. Different models including Guoy Chapman model, Stern model and classical model have been considered in unit 2

Study unit 1 (Module 2) considers polarization at electrochemical interphases. Polarization of single and complete electrodes is considered. Different types of polarization and their implications have also been singled out and discusses. Diagrams have been presented in order to facilitate ease of understanding. Models governing concentration, activation and total polarizations have been derived and discussed. The unit is simplified by analysing some typical examples obtained from other studied.

Study 2 (Module 2) attempt to verified Tafel law, which is simplified by derivation of Butler Volmer equation. Applications of the equation in practical fields are presented, in a form, that should be understood by the student.

Study unit 1 (Module 3) examines mass transport. Diffusion, convection and migration are identified as the three major ways of mass transport in electrochemical interphases. Derivation of Fick's law and their implication has been extended in order to simplified diffusion as a

means of mass transport. Migration has also been singled out and discussed and the equation connecting the three-mass transport process has been presented and discussed.

The science of polarography, its principles, application and theory have been carefully presented in Study Unit 2 (Module 3). The basic features of polarogram, which is the half wave potential has been discusses in details. Diagrams are presented to aid the students' comprehension and understanding of polarography.

In Study 3 of Module 3, electronics is highlighted as fundamental needs in electrochemistry. Some circuits elements have been highlighted and practical circuits diagram in some electrochemical analysis has also been presented.

REFERENCES AND FURTHER READINGS

Textbooks referred to in the development of each units are presented at the end of the units. However, list of some General references is presented below:

Atkins, P. and De Paula, J. (2010). *Atkins 'Physical chemistry*. 9th Edition. Oxford University Press. UK.

Barsukov, V. Z., Borysenko, Y. V., Linyucheva, O. V., Senyk, I. V. and Khomenko, V.G. (2017). *Promising Materials and Processes in Applied Electrochemistry*. Kyiv National University of Technologies and Design, Ukraine. ISBN: 978-966-7972-79-0

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Monk, P. (2004). *Physical chemistry: Understanding the Chemical World*. John Wiley and Sons Ltd. England.

Onuchukwu, A. I. (2008). *Electrochemical technology*. Spectrum Books Limited. Nigeria.
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Popov, K. I., Djokic, S. S., Nikolic, N. D. and Jovic, V. D. (2016). *Morphology of electrochemically and chemically deposited metals*. Springer International Publishing, USA. ISBN: 978-3-319-26071-6

Scholz, F. (2017). *Electrochemistry in a divided world. Innovations in Eastern Europe in the* 20th Century. Springer, UK. ISBN: 978-3-319-21220-3, (e-book ISBN 978-3-319-21221-0)

Zamec, Z. (2004). *Electrochemistry at the interface between two immiscible electrolyte solutions* (IUPAC Technical Report). *Pure and Applied Chemistry* 76(12);2147–2180.

Link to slide show:https://www.slideshare.net/GamryInstruments/echem-basics-for-users

PRESENTATION SCHEDULE

This course is presented in three different modules. Each module consists of two study units. Each module begins with introduction, study outcomes and main content. Within the main content, fundamental facts are presented along with inline worked examples and answers. Each unit ends with summary, conclusion, bibliography, self assessment questions/answers and activity for student to test their comprehension.

ASSESSMENT

There are two aspects of assessment for this course: the tutor-marked assignment (TMA) and end of course examination. The TMAs shall constitute the continuous assessment component of the course. They will be marked by the tutor and equally account for 30 % of the total course score. Each learner shall be examined in four TMAs before the end of course examination. The end of course examination shall constitute 70% of the total course score.

HOW TO GET THE MOST FROM THE COURSE

Student are expected to comprehends best information out of this course through careful study of each units. It is recommended that student should test their ability to answer questions that follow each unit as well as questions in reference materials related to this course

MAIN COURSE

MODULE 1

STUDY UNIT 1: ELECTROCHEMICAL SYSTEMS

1.0 Introduction

2.0 Intended Learning Outcomes

3.0 Main Content

- **3.1 Electrochemical cells**
  - **3.1.1 Types of electrochemical cells**
  - **3.1.2 Electrode potential**
- **3.2 Types of interphase in electrochemistry**
  - **3.2.1 Metal Solution interphase**
  - **3.2.2 Metal-metal interphase**
  - **3.2.3 Solution-solution interphase**

4.0 (i) Self Assessment Exercise and Answers

(ii) Class Activity

5.0 Conclusion

6.0 Summary

7.0 References/Further Readings

MODULE 1

STUDY UNIT 2: ELECTRIC DOUBLE LAYER

1.0 Introduction

2.0 Intended Learning Outcomes

3.0 Main Content

- **3.1 Over view of the electric double layer**
  - **3.1.1 The double layer models**
  - **3.1.2 Application of electric double layer**
- **3.2 Potential at zero charge**

4.0 (i) Self Assessment Exercise and Answers

(ii) Class Activity

5.0 Conclusion

6.0 Summary

7.0 References/Further Readings

MODULE 2

STUDY UNIT 1: POLARIZATION AT INTERPHASE

1.0 Introduction

2.0 Intended Learning Outcomes

3.0 Main Content

3.1 Polarization at the interface

3.1.1 Polarizable and non polarizable interphases

3.1.2 Polarization of a single electrode

3,2 Dependent of activation overpotential on current

3,2 The Nernst equation

4.0 (i) Self Assessment Exercise and Answers

(ii) Class Activity

5.0 Conclusion

6.0 Summary

7.0 References/Further Readings

MODULE 2

STUDY UNIT 2: VERIFICATION OF TAFEL EQUATION: BUTLER VOLMER LAW

1.0 Introduction

2.0 Intended Learning Outcome

3.0 Main Content

3.1 Derivation of Butler Volmer equation

3.2 Experimental determination of current and Tafel plot

3.2.1 Significance of Tafel plot

3.3 Concentration potential

3.4 Total overpotential

4.0 (i) Self Assessment Exercise and Answers

(ii) Class Activity

5.0 Conclusion

6.0 Summary

7.0 References/Further Reading

MODULE 3

STUDY UNIT 1: MASS TRANSPORT

1.0 Introduction

2.0 Intended Learning Outcomes

3.0 Main Content

3.1 Transportation in electrochemical systems

3.1.1 Mass transport

3.1.2 Ion transport and conductivity

3.2 Ostwald dilution law

3.3 Ionic atmosphere and Onsager equation

3.4 The law of the independent migration of ions

3.5 Kohlrausch law

3.6 Ionic activity

3.7 Migration of ion in electrolyte

3.8 Determination of solubility by conductance measurements

3.9 Conductivity titrations

3.10 Electrolytic cell and electrolysis

3.11 Rotating disk electrode (RDE) theory: the Levich equation

4.0 (i) Self Assessment Exercise and Answers

(ii) Class Activity

5.0 Conclusion

6.0 Summary

7.0 References/Further Reading

MODULE 3

STUDY UNIT 2:POLAROGRAPHY

1.0 Introduction

2.0 Learning Outcome

3.0 Main Content

3.1 Theory and principles of polarography

3.1.1 Diffusion current

3.1.2 The half wave potential and its significance

4.0 (i) Self Assessment Exercises and Answer

(ii) Class Activity

5.0 Conclusion

6.0 Summary

7.0 References/Further Readings

MODULE 3

STUDY UNIT 3: ELECTRONICS IN ELECTROCHEMISTRY

1.0 Introduction

2.0 Intended Learning Outcomes

3.0 Main Content

- **3.1 Electronics and instrumentation**
- **3.2 Transducer and detector**
- **3.3 Electrochemical circuit**
- **3.4 Polarization circuit**
- **3.5 Circuits for emf measurements**
- **3.6 Electrochemical impedance spectroscopy**

4.0 (i) Self Assessment Exercises and Answers

(ii) Class Activity

5.0 Conclusion

6.0 Summary

7.0 References/Further Readings

MODULE 1

STUDY UNIT 1: ELECTROCHEMICAL SYSTEMS

2.0 Introduction

2.0 Intended Learning Outcomes

3.0 Main Content

3.1 Electrochemical cells

3.1.1 Types of electrochemical cells

3.1.2 Electrode potential

3.2 Types of interphase in electrochemistry

3.2.1 Metal Solution interphase

3.2.2 Metal-metal interphase

3.2.3 Solution-solution interphase

4.0 (i) Self Assessment Exercise and Answers

(ii) Class Activity

5.0 Conclusion

6.0 Summary

7.0 References/Further Readings

1.0 Introduction

Electrochemistry is concerned with the study of interaction between electrical and chemical effects. This implies that chemical energy can be converted into electrical energy and vice versa. Every electrochemical system must have the electrodes (cathode and anode) and the electrolytes. It has been found that an electrochemical system is not homogenous but heterogeneous systems. Therefore, there exists certain regions call interphase within electrochemical systems.

An electrochemical system can also be defined as a system in which there is a difference of electric potential between two or more phases. The difference in potentials can arise in several ways but the significant ones are

i. Charge transfer between metal solution interphase
ii. Charge transfer between metal-metal interphase
iii. Charge transfer between solution-solution interphase

The magnitude of the potential controls the direction and the rate of charge transfer between electrochemical interphase. The study of charge transfer at the interphase is significant because most advantages and applications that can be gotten from electrochemical systems resides or position themselves within the interphase. Therefore, this section shall examine the various

electrochemical interphases and how they are positioned or organised within an electrochemical system.

3.0 Intended Learning Outcomes

When you have studied this session, you should be able to:

i. Introduce and explain the different types of interphases in electrochemistry
ii. Explain the concept of charge transfer through interphases
iii. Highlight factors that influence complex distribution of electric charge in interphases
iv. Use suitable diagrams to explain metal-metal and metal–solution interphases

3.0 Main Content

3.1 Electrochemical cell

An electrochemical cell generally consists of two half-cells, each containing an electrode in contact with an electrolyte. The electrode is an electronic conductor (such as a metal or carbon) or a semiconductor. Current flows through the electrodes via the movement of electrons. An electrolyte is a phase in which charge is carried by ions. Normally, positive ions move toward the negative electrode while negative ions move toward the positive electrode. The movement of electrons is from the anode to the cathode in a galvanic cell and vice versa. Therefore, electrochemical cells operate through the movement of ions or electrons, generated within the system. The movement of electrons within an electrochemical cell occurs via oxidation and reduction processes (i.e. redox reaction). Oxidation involves loss of electron while reduction involves gain of electron. The chemical specie that is oxidized is called a reducing agent while the chemical specie that is reduced is called an oxidizing agent. For example, the reaction involving H_2 and Cl_2 can be written as,

$$H_2 + Cl_2 \rightarrow 2HCl$$

The oxidation reaction is: $H_2 \rightarrow 2H^+ + 2e^-$

The reduction reaction is: $Cl_2 + 2e^- \rightarrow 2Cl^-$

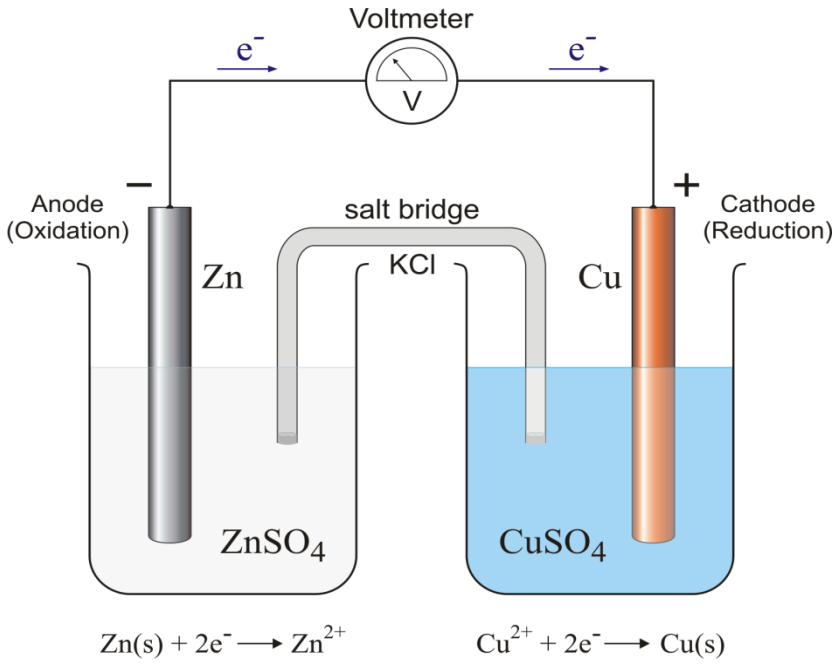
The overall reaction is: $H_2 + Cl_2 \rightarrow 2H^+ + 2Cl^-$

From the above, it is evident that the oxidation number of H_2 changes from zero to +1 while that of Cl_2 changes from zero to -1. Therefore, 1 mole of H_2 loses two electron and become oxidized while one mole of Cl_2 accept the two electrons and become reduced. H_2 is the reducing agent while Cl_2 is the oxidizing agent. The oxidizing reaction constitutes one half cell reaction while the reduction constitutes the other half cell reaction. The sum of two half cells is the overall cell reaction.

3.1.1 Types of electrochemical cell

Chemical reactions taking place in an electrochemical cell is essentially a redox reaction. An electrochemical cell is an assemble of two electrodes (negative electrode called anode and positive electrode called the cathode), an electrolyte and a medium that connects the anode and the cathode together. Electrochemical cells can broadly be classified into Galvanic cell and electrolytic cell.

3.1.1.1 In galvanic cells (Fig. 1.1) reactions occur spontaneously at the electrode/electrolyte interfaces when the two electrodes are connected by a conductor such as a metal wire. Galvanic cells convert chemical energy to electric energy and are the components of batteries, which usually contain several cells connected in series. In galvanic cell, the half cells are set up in different containers and each cell is joined by a salt bridge, a porous plug. The salt bridge is a separator that allows ions to move between the half-cells but prevents mixing of the electrolytes. The separator can also be a tube of aqueous solution plugged at both ends with glass wool, or it can be an ion exchange membrane or a sintered-glass disk. In galvanic cell, the anode is negative and the cathode is positive. In the galvanic cell, electrons are supplied by the oxidizing specie.



$$Zn(s) \mid ZnSO_4(aq) \,||\, CuSO_4(aq) \mid Cu(s)$$

Fig.1.1: Diagram of a Zn-Cu galvanic cell

In electrolytic cells (Fig. 2 and 3), reactions are not spontaneous but are forced to occur at the electrode/electrolyte interfaces by way of an external source of power connected to both electrodes. The external battery supplies the electrons, which enters the cell through the cathode. The anode in this case is the positive electrode while the cathode is the negative

electrode. Electric energy from the external source is converted to chemical energy in the form of the products of the electrode reaction. In an electrolytic cell, both electrodes are placed in the same compartment containing the molten solution of the electrolyte. Fig.1.2 shows electrolytic cell with electrodes made from different materials while Fig.1.3 shows electrochemical cell with two electrodes, made from the same materials (i.e. copper)

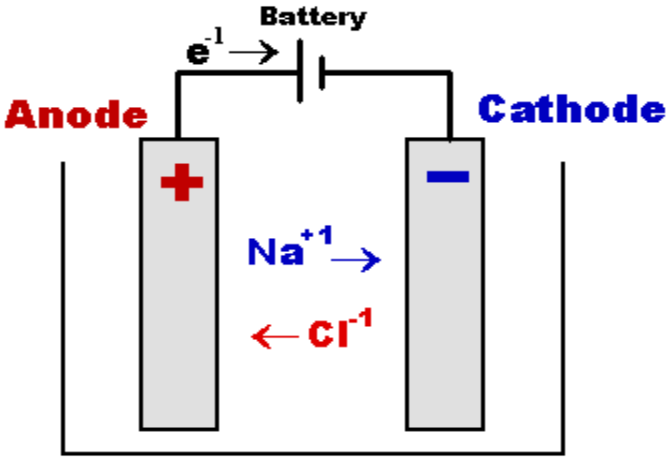


Fig.1.2: Diagram of an electrolytic cell

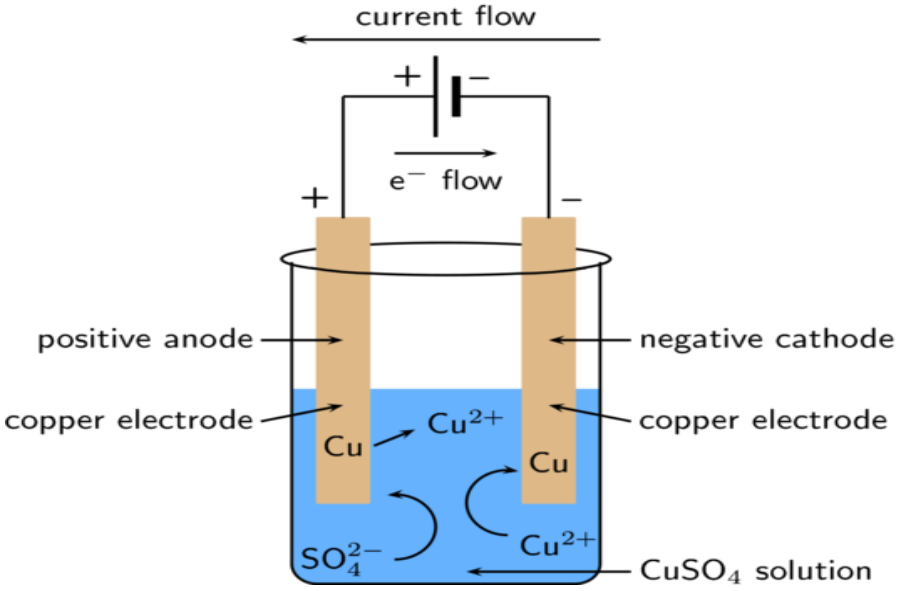


Fig.1.3: Diagram of an electrolytic cell with Cu as the anode and cathode.

Worked example 1

(a) With the aid of suitable diagrams, highlight and differentiate the basic features of electrolytic cell and galvanic cell.

(b) What is salt bridge and its significant in a galvanic cell?

Solution

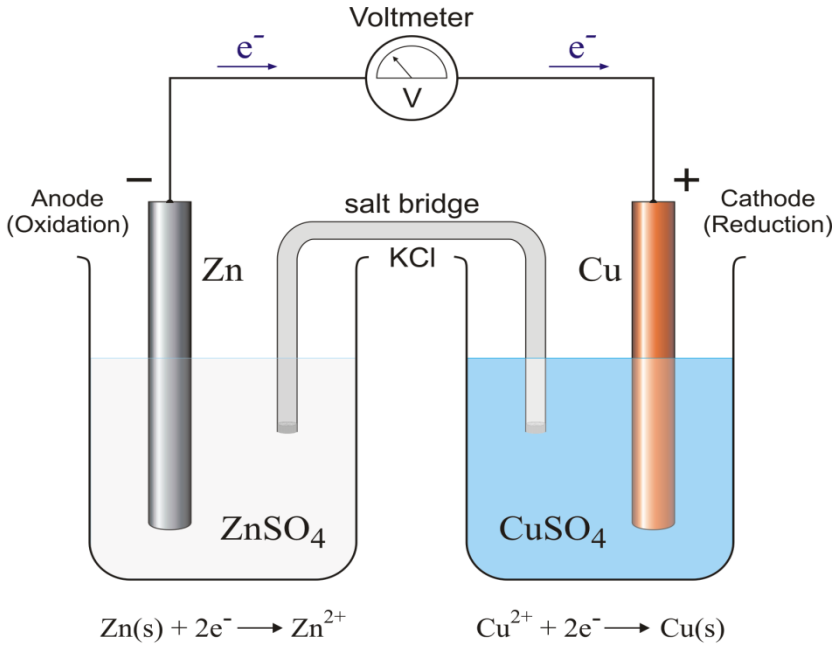
(a) Galvanic cell

i. In galvanic cells (**Fig.1.4**) reactions occur spontaneously at the electrode/electrolyte interfaces when the two electrodes are connected by a conductor such as a metal wire.

ii. Galvanic cells convert chemical energy to electric energy

iii. In galvanic cell, the half cells are set up in different containers and each cell is joined by a salt bridge, a porous plug.

iv. In galvanic cell, the anode is negative and the cathode is positive. Electrons are supplied by the oxidizing specie.



$$Zn(s) \mid ZnSO_4(aq) \,||\, CuSO_4(aq) \mid Cu(s)$$

Fig. 1.4: Diagram of a Zn-Cu galvanic cell

Electrolytic cell

i. In electrolytic cells (**Figs. 1.5a and 51. b**), reactions are not spontaneous but are forced to occur at the electrode/electrolyte interfaces by way of an external source of power connected to both electrodes.

ii. The external battery supplies the electrons, which enters the cell through the cathode.

iii. The anode in this case is the positive electrode while the cathode is the negative electrode.

iv. Electric energy from the external source is converted to chemical energy in the form of the products of the electrode reaction.

v. In an electrolytic cell, both electrodes are placed in the same compartment containing the molten solution of the electrolyte.

vi. Fig. 2 shows electrolytic cell with electrodes made from different materials while Fig. 3 shows electrochemical cell with two electrodes, made from the same materials (i.e. copper)

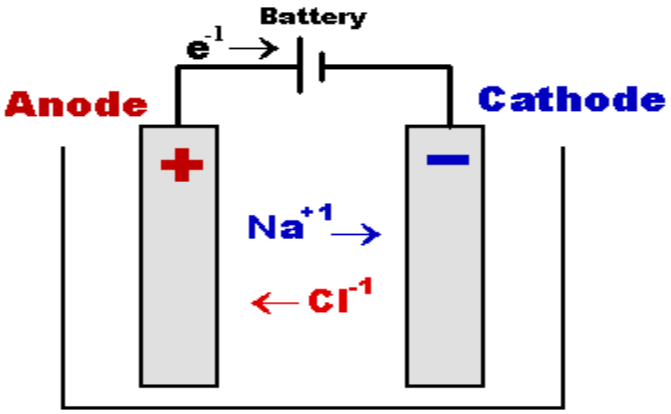


Fig.1.5a: Diagram of an electrolytic cell

(b) The salt bridge is a separator that allows ions to move between the half-cells but prevents mixing of the electrolytes. The separator can also be a tube of aqueous solution plugged at both ends with glass wool, or it can be an ion exchange membrane or a sintered-glass disk.

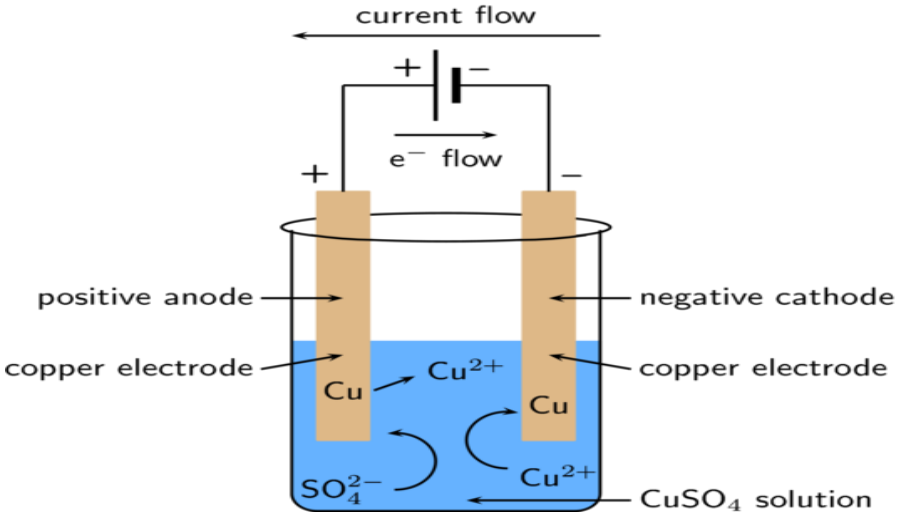


Fig.1.5b: Diagram of an electrolytic cell with Cu as the anode and cathode.

3.1.1.2 Construction of galvanic cell

A galvanic cell consists of two half cells that are electrically connected. Each half cell is positioned in the electrochemical cell such that a half reaction will takes place. A single half-cell can be made up of a metallic strip that dips into a solution of the metal ion (egg. Zn-Zn ion half-cell, called zinc electrode) consist of zinc metal strip dipped into a solution of zinc salt or a copper metal strip dipped into a solution (Cu electrode). In the cell, the two-half cell are

connected in such a way that electron flow from one metal electrode to another through cell connection. Consider a cell consisting of Zn and copper electrodes. Zinc tends to lose electron more easily than copper; it will take up charge relative to copper electrode. When the two electrodes are connected through external metallic wire, electrons flow from the zinc through the external circuit to the copper. The following half reactions occur,

$$Oxidation: Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$$

$$Reduction: Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$$

The first half reaction occurs at the anode and reveals that Zn metal oxidizes to Zn^{2+} which goes into solution while the second half cell reaction indicates that copper ion gained two electrons from zinc to form Cu metal. The two half-cell needs to be connected internally or externally to allow e^- to pass through them. As Zn^{2+} continues to be produced the Zn ion begins to build up positive charges and the copper, negative charges. Consequently, the solution containing Zn(s) becomes more positively charged as the solution containing Cu(s) becomes more negatively charged. For the voltaic cell to operate effectively, the solutions in the two half-cells must remain electrically neutral. Therefore, a salt bridge containing KNO_3 is added to keep the solutions neutral by adding NO_3^-, an anion, into the anode solution and K^+, a cation, into the cathode solution. As oxidation and reduction proceed, ions from the salt bridge migrate to prevent charge build up in the cell compartments. The overall cell reaction is,

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

An equation of this nature, which represents the combination of two half cells reactions can be represented by a notation called, cell notation. For example, the cell notation for the above reaction is,

$$Zn_{(s)}|Zn^{2+}_{(aq)}\|Cu^{2+}_{(aq)}|Cu_{(s)}$$

The double vertical line is used to separate the cathodic half reaction from the anodic half reaction. The oxidation cell is placed on the left, while the reduction cell is placed on the right. The single vertical line is used to separate different state of matter on the same side. If the state of matter is the same on the same side, then comma will be used. For example,

$$Fe^{2+}_{(aq)}, Fe^{3+}_{(aq)}\|Ag^{+}_{(aq)}|Ag_{(s)}$$

3.2 Electrode potential

Electrode potential of a cell is defined as the potential of the cell in which the anode is the standard hydrogen electrode and the cathode is the electrode of the cell. In an electrochemical cell, oxidation takes place at the anode while reduction takes place at the cathode. According to the IUPAC convention, electrode potential is the electromotive force of a cell built from two

electrodes such that on the left-hand side is the standard hydrogen electrode and on the right-hand side is the electrode the potential is being defined.

$$E *_{cell} = E_{cathode} - E_{anode} \quad 1.3$$

$$E_{cell} = E_{right} - E_{left} \quad 1.4$$

The convention also assumes that at a pressure, $p(H_2)$ = 101325 Pa and at activity, $a(H^+)$ = 1.00 the electrode potential of standard hydrogen electrode is 0.000 V, therefore,

$$E_{cell} = E_{cathode} - o = E_{electrode}$$

However, the actual potential of hydrogen electrode at 25° C is 4.44 ± 0.02 V. For example, the cell notation for an electrochemical assembly for measuring the electrode potential of zinc can be written as,

$$Pt_{(s)}|H_{2(g)}|H^+_{(aq)}\|Zn^{2+}_{(aq)}|Zn_{(s)}$$

The half-cell reactions for the above cell are,

$$Reduction: \quad 2H^+_{(aq)} + 2e^- = H_{2(g)}$$

$$Oxidation: Zn_{(s)} = Zn^{2+}_{(aq)} + 2e^-$$

$$\boldsymbol{Overall reaction (summation of the two): 2H^+_{(aq)} + Zn_{(s)} = H_{2(g)} + Zn^{2+}_{(aq)}}$$

Fig.1.6 shows an electrochemical assembly for measuring the electrode potential of magnesium. It can be seen in the arrangement that the concentration of Mg^{2+} and that of the H^+ is equal to 1 mol/dm^3. The standard hydrogen electrode is seen to consist of a glass that envelop a platinum foil covered by porous platinum and containing hydrogen gas maintained at a pressure of 1 bar. The entire system is dipped into a solution of tetraoxosulphate (VI) acid.

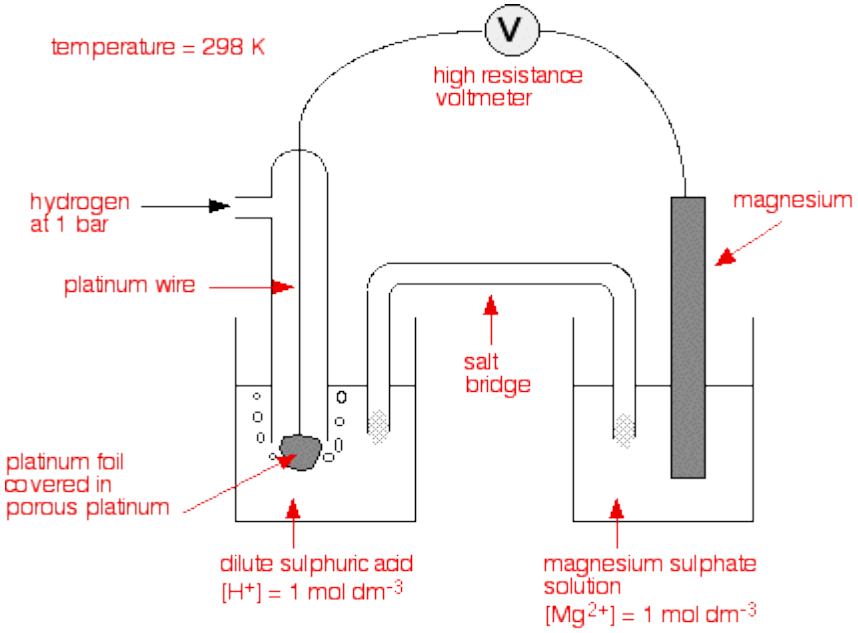


Fig. 1.6: An electrochemical assembly for measuring the electrode potential of magnesium

It is significant to state that the direction of electron flow depends on the electrode potential of the measured electrode with respect to that of the standard hydrogen electrode. Generally, electron flows from the more negative electrode to the other electrode. For example, Fig.1.7 shows an electrochemical assembly for measuring the electrode potential of copper.

From the diagram, the cell notation can be written as, $Pt_{(s)}|H_{2(g)}|H^{+}_{(aq)}\|Cu^{2+}_{(aq)}|Cu_{(s)}$

The measured potential is + 0.34 V which is more positive than that of the standard hydrogen electrode (the reference electrode), whose potential is 0.000 V. Therefore, electron will flow from hydrogen electrode to the copper electrode and the half-cell reactions will be,

$$H_{2(g)} \;=\; 2H^{+}_{(aq)} \;+\; 2e^{-}$$

$$Cu^{2+}_{(aq)} + \;2e^{-} \;=\; Cu_{(s)}$$

The overall cell reaction is $H_{2(g)} + Cu^{2+}_{(aq)} \;=\; 2H^{+}_{(aq)} + \;Cu_{(s)}$. Therefore, the standard electrode potential of the cell can be expressed as,

$$E^{0}_{cell} \;=\; E^{0}_{+ve/red} - E^{0}_{-ve/oxid} \;=\; E^{0}_{Cu^{2+}/Cu} - E^{0}_{H^{+}/H_2} = 0.34 - (-0.00) = 0.34\,V$$

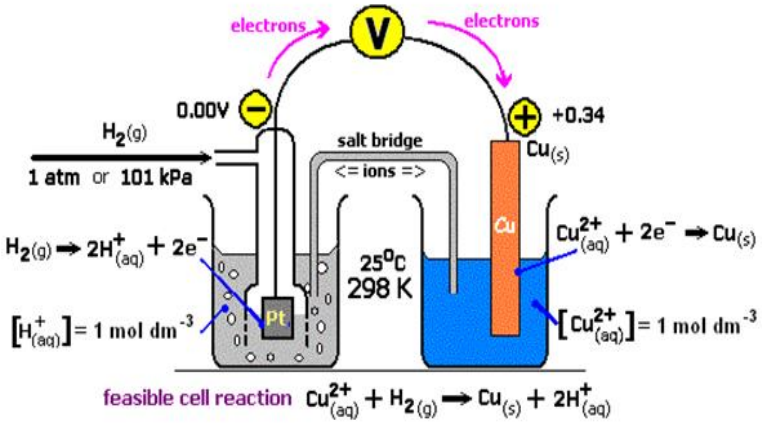


Fig. 1.7: Electrochemical cell for measuring the standard electro potential of copper electrode

The actual cell notation for the above system (i.e. IUPAC convention) is the same as the one suggested by the diagram, $Pt_{(s)}|H_{2(g)}|H^{+}_{(aq)}\|Cu^{2+}_{(aq)}|Cu_{(s)}$. The change in electrode potential from the equilibrium potential (i.e. polarization) is cause by the build-up of the cell reaction products, H^{+} ions from the oxidation of the hydrogen gas and the decrease in the concentration of Cu^{2+} as a result of reduction to copper.

The second case can be understood by examining the half reactions that are initiated when an electrochemical assembly is set up for measuring the electrode potential of zinc as shown in Fig. 1.8. The cell notation to match the diagram is

$$Pt_{(s)}|H_{2(g)}|H^{+}_{(aq)}\|Zn^{2+}_{(aq)}|Zn_{(s)}$$

Experimental evidence reveals that the measured standard potential for this system is -0.76 V, which indicate that the potential is more negative than that of the standard hydrogen electrode. Therefore, electron will flow from zinc electrode to the hydrogen electrode and the electrode potential of the cell can be written as,

$$E^0_{cell} = E^0_{-ve/oxid} - E^0_{+ve/red} = E^0_{Zn^{2+}/Zn} - E^0_{H^+/H_2} = -0.76 - 0.00 = -0.76\,V$$

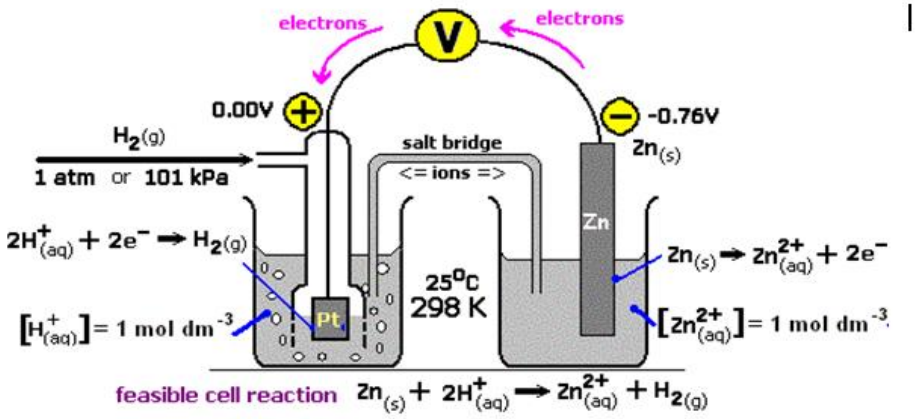


Fig. 1.8: Electrochemical cell for measuring the standard electro potential of zinc electrode

The half reactions and the overall cell reaction are,

$$Reduction: \quad 2H^+_{(aq)} + 2e^- = H_{2(g)}$$

$$Oxidation: Zn_{(s)} = Zn^{2+}_{(aq)} + 2e^-$$

$$\boldsymbol{Overall\ reaction\ (summation\ of\ the\ two): 2H^+_{(aq)} + Zn_{(s)} = H_{2(g)} + Zn^{2+}_{(aq)}}$$

Therefore, the actual cell notation is

$$Zn_{(s)}\left|Zn^{2+}_{(aq)}\right\|H^+_{(aq)}\left|H_{2(g)}\right|Pt_{(s)}$$

In this case, the change in electrode potential from the equilibrium potential (i.e. polarization) is caused by the build-up of the cell reaction products including zinc ions from the oxidation of zinc electrode and the decrease in concentration of hydrogen ions due to their reduction to H_2.

It is seen from the above example that the sign of the value of the standard electro potential of the metal determines the direction of flow of electron. If two electrode systems such as copper and zinc are coupled together (Fig. 1.9), it is evidence from the values of their electrode potentials (E^0 = +0.34 V and -0.76 V for copper and zinc respectively) that electron will flow from zinc electrode through copper electrode to the cell because the standard electrode potential of zinc is more negative than that of copper. This implies that zinc will act as the anode while copper will act as the cathode. The anodic and cathodic half reactions are as follows,

$$Anodic\ half\ reaction\ (oxidation): Zn_{(s)} = Zn^{2+}_{(aq)} + 2e^-$$

$$Cathodic\ half\ reaction\ (reduction): Cu^{2+}_{(aq)} + 2e^- = Cu_{(s)}$$

$$\boldsymbol{Overall\ reaction: Zn_{(s)} + Cu^{2+}_{(aq)} = Zn^{2+}_{(aq)} + Cu_{(s)}}$$

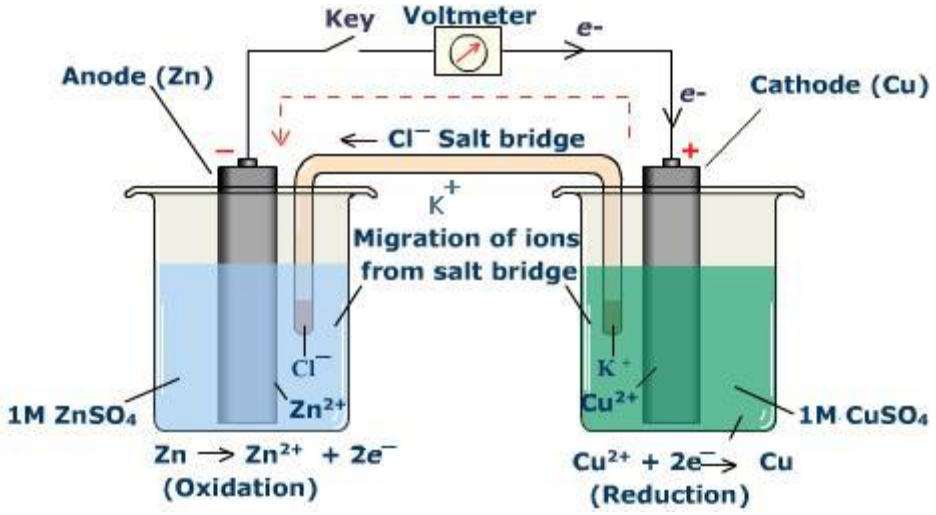


Fig. 1.9: Zinc- copper electrochemical cell

From thermodynamic point of view, a cell reaction is spontaneous when the standard free energy change is negative. The relationship between the standard free energy change and electrode potential can be written as,

$$\Delta G^0 = -nFE^0_{cell} \qquad 1.5$$

where ΔG^0 is the standard free energy change, n is the number of electrons, F is the Faraday and E^0 is the electrode potential of the cell. The standard electrode potential of the cell can be calculated as follows,

$$E^0_{cell} = E^0_{cathode} - E^0_{anode} = 0.34\ V - (-0.76\ V) = 1.10\ V$$

This implies that the standard free energy change of the cell is given as,

$$\Delta G^0 = -2\ x\ 96500\ C\ x\ 1.10\ V = -212,300\ J$$

Since the standard free energy change is negative, it means that the cell reaction is spontaneous. Therefore, for an electrochemical reaction to be spontaneous, the standard electrode potential of the cell must be positive.

In electrochemistry, the basic types of electrode potentials are galvanic potential, Volta potential and surface potential. Galvanic potential is also called inner potential and is denoted by the symbol, Φ. Galvanic potential is the work required to move a unit charge from infinity to a given phase. Volta potential or outer potential is denoted by Ψ. It is the electric potential of an electrical charged body, defined as the work required to move a unit electric charge to a

distant (approximately a thousand nanometer, outside the phase) that is very close to the phase. Surface potential (χ) is the work required to pass initial charge across the surface layer. Surface potential is majorly contributed by the electric double layer.

The sum of the Volta and surface potential gives the Galvani potential. Therefore,

$$\Phi = \Psi + \chi \qquad 1.6$$

The Volta potential between two electrodes can be easily measured but the galvanic potential cannot be easily measured. However, Galvani potentials are very significant because the true electrode potential is the difference between the Galvani potentials of the electrode phase and the electrolyte phase.

Worked example 2

(a) Draw suitable diagrams to show how the standard electrode potential of copper and zinc can be measured,

(b) Discuss the electrochemistry of the expected and actual direction of electron flow in each of the cells in (a) above. Write the expected and actual cell notation for each of them.

(c) What are the expected causes of polarization in each of the cell?

(d) If the two electrode systems are coupled together, answer the following questions,

(i) Draw a cell diagram to show the expected arrangement

(ii) Write equations for the cathodic, anodic and overall cell reactions

(iii) Calculate the electrode potential of the coupled cell

(iv) Show that the electrode reaction for the coupled cell is spontaneous. Hence state the condition required for an electrochemical reaction to be spontaneous.

Solution

(a) The cell diagrams are given in Figs. 1.10 and 1.11 respectively.

From Fig. 1.10, the diagram, the cell notation can be written as, $Pt_{(s)}|H_{2(g)}|H^{+}_{(aq)}\|Cu^{2+}_{(aq)}|Cu_{(s)}$. The measured potential is + 0.34 V which is more positive than that of the standard hydrogen electrode (the reference electrode). Therefore, electron will flow from hydrogen electrode to the copper electrode and the half-cell reactions will be,

$$H_{2(g)} = 2H^{+}_{(aq)} + 2e^{-}$$

$$Cu^{2+}_{(aq)} + 2e^{-} = Cu_{(s)}$$

The overall cell reaction is $H_{2(g)} + Cu^{2+}_{(aq)} = 2H^{+}_{(aq)} + Cu_{(s)}$. Therefore, the standard electrode potential of the cell can be expressed as,

$$E^{0}_{cell} = E^{0}_{+ve/red} - E^{0}_{-ve/oxid} = E^{0}_{Cu^{2+}/Cu} - E^{0}_{H^{+}/H_2} = 0.34 - (-0.00) = 0.34\,V$$

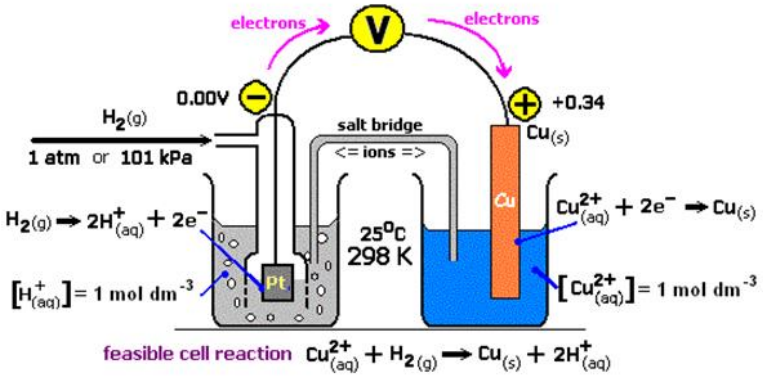


Fig. 1.10: Electrochemical cell for measuring the standard electro potential of copper electrode

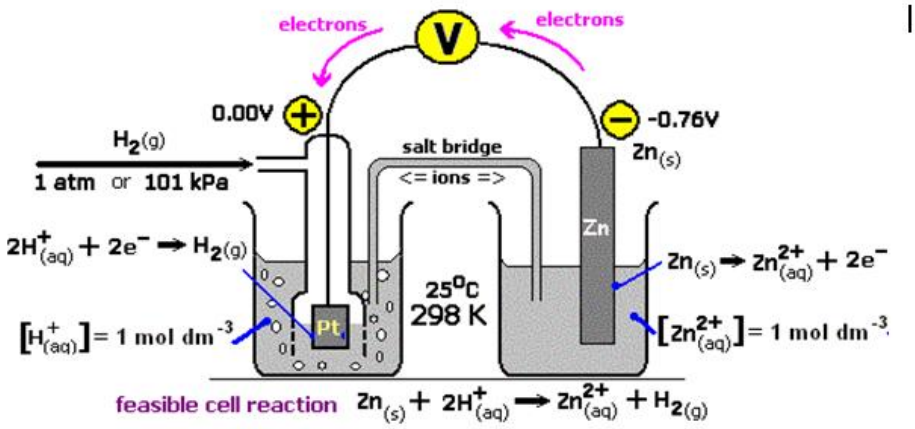


Fig. 1.11: Electrochemical cell for measuring the standard electro potential of zinc electrode

The actual cell notation for the above system (i.e. IUPAC convention) is the same as the one suggested by the diagram, $Pt_{(s)}|H_{2(g)}|H^+_{(aq)}\|Cu^{2+}_{(aq)}|Cu_{(s)}$.

The second case can be understood by examining the half reactions that are initiated when an electrochemical assembly is set up for measuring the electrode potential of zinc as shown in Fig. 1.11. The cell notation to match the diagram is

$$Pt_{(s)}|H_{2(g)}|H^+_{(aq)}\|Zn^{2+}_{(aq)}|Zn_{(s)}$$

The measured standard potential for this system is -0.76 V, which indicate that the potential is more negative than that of the standard hydrogen electrode. Therefore, electron will flow from zinc electrode to the hydrogen electrode and the electrode potential of the cell can be written as,

$$E^0_{cell} = E^0_{-ve/oxid} - E^0_{+ve/red} = E^0_{Zn^{2+}/Zn} - E^0_{H^+/H_2} = -0.76 - 0.00 = -0.76\,V$$

The half reactions and the overall cell reaction are,

$$Reduction: \quad 2H^+_{(aq)} + 2e^- = H_{2(g)}$$

$$Oxidation: Zn_{(s)} = Zn^{2+}_{(aq)} + 2e^-$$

$$\boldsymbol{Overall\ reaction\ (summation\ of\ the\ two): 2H^+_{(aq)} + Zn_{(s)} = H_{2(g)} + Zn^{2+}_{(aq)}}$$

Therefore, the actual cell notation is

$$Zn_{(s)}\left|Zn^{2+}_{(aq)}\right\|H^+_{(aq)}\left|H_{2(g)}\right|Pt_{(s)}$$

(c) The change in electrode potential from the equilibrium potential (i.e. polarization) is cause by the build-up of the cell reaction products, H^+ ions from the oxidation of the hydrogen gas and the decrease in the concentration of Cu^{2+} as a result of reduction to copper. In the case of zinc, the change in electrode potential from the equilibrium potential (i.e. polarization) is caused by the build-up of the cell reaction products including zinc ions from the oxidation of zinc electrode and the decrease in concentration of hydrogen ions due to their reduction to H_2.

(d) (i) The cell diagram is given in Fig. 1.12

(ii) The anodic, cathodic and overall reactions are,

$$Anodic\ half\ reaction\ (oxidation): Zn_{(s)} = Zn^{2+}_{(aq)} + 2e^-$$

$$Cathodic\ half\ reaction\ (reduction): Cu^{2+}_{(aq)} + 2e^- = Cu_{(s)}$$

$$\boldsymbol{Overall\ reaction: Zn_{(s)} + Cu^{2+}_{(aq)} = Zn^{2+}_{(aq)} + Cu_{(s)}}$$

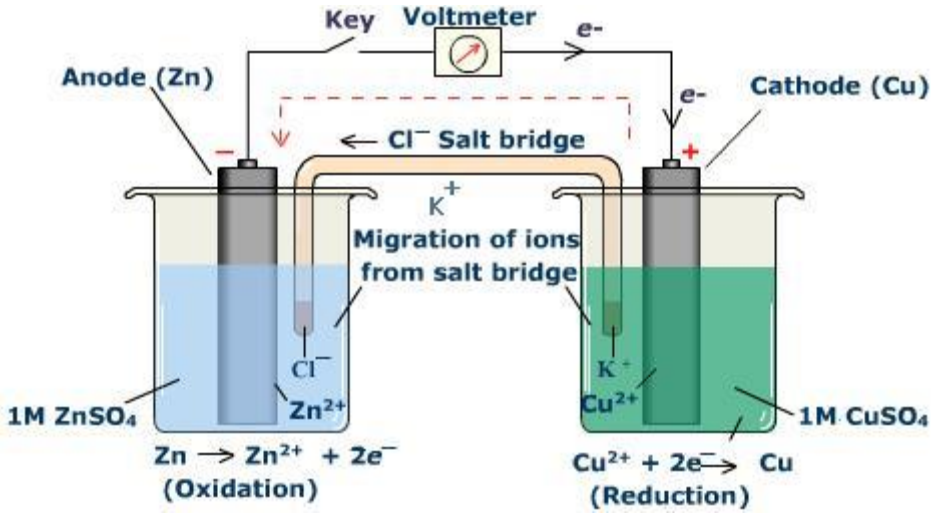


Fig. 1.12: Zinc- copper electrochemical cell

(iii) The standard electrode potential of the cell can be calculated as follows,

$$E^0_{cell} = E^0_{cathode} - E^0_{anode} = 0.34\,V - (-0.76\,V) = 1.10\,V$$

(iv) From thermodynamic point of view, a cell reaction is spontaneous when the standard free energy change is negative. The relationship between the standard free energy change and the standard electrode potential can be written as,

$$\Delta G^0 = -nFE^0_{cell}$$

where ΔG^0 is the standard free energy change, n is the number of electrons, F is the Faraday and E^0 is the electrode potential of the cell. This implies that the standard free energy change of the cell is given as,

$$\Delta G^0 = -2\ x\ 96500\ C\ x\ 1.10\ V = -212,300\ J$$

Since the standard free energy change is negative, it means that the cell reaction is spontaneous. Therefore, for an electrochemical reaction to be spontaneous, the standard electrode potential of the cell must be positive.

Worked example 3

(a) Highlight the effect of size and charge of ions, Coulombic interaction and ion pair on conductivity

(b) With the aid of suitable diagram, highlight the basic properties of the three basic types of ion pair

Solution

(a) Conductivity in electrolyte is due to mobility of ions. When a salt is dissolved in water, the energy required, is provided by hydration. The extent of hydration depends on the size and charge of the ion. A small highly charged ion such as K^+ will be easily hydrated than Al^{3+}, which has higher size and charge. Hydrated ions of opposite charge show little tendency to attract ion in aqueous solution because the high permittivity (ε) of water reduces the force (i.e, F) between charges, q_1 and q_2. For two oppositely charge ions with magnitudes, q_1 and q_2, the columbic interaction between them is given as,

$$F = \frac{q_1 q_2}{4\pi l^2 \varepsilon}$$

where l is the distant of separation between the charges. ε is the dielectric constant of the solvent.ε= 78.54 for water at 298 K.

Worked example 4

Calculate the force between two charges of magnitude, 1.2 and 1.6 C separated by a distant of 0.8 m in a medium whose relative permittivity is 78.54 at 298 K

Solution

The force is given as

$$F = \frac{q_1 q_2}{4 \in \pi l^2}$$

Given, q_1 = 1.2 C, q_2 = 1.6 C, l = 0.8 m and $\in = 78.54$

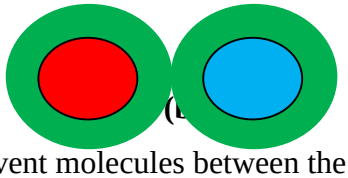
$F = \frac{(1.2)(1.6)(7)}{4(78.54)(22)(0.8)^2} = 0.003084\ N$

Another factor that may also affects the conductivity of an electrolyte solution is the association of water molecule with ions (i.e. formation of hydration sheath). This is capable of inhibiting ionic association and can hinder conductivity. For example, at high concentration, Mg^{2+} and SO_4^{2-} associate according to the following equation:

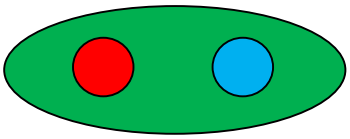
$$Mg^{2+} + SO_4^{2-} = Mg^{2+}SO_4^{2-}$$

This association can hinder the conductivity of the electrolyte because ions pairs do not conduct electricity.

(b) Ion pair can be classified as fully solvated, solvent-shared/solvent-separated and contact ion pair. In the Figure below, the solvent is coloured green while the cation and the anion are coloured red and light blue respectively. The diagram represents fully solvated ion pair because both ions (cation and anion) have complete solvation sphere

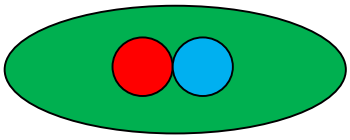


However, when there are one solvent molecules between the cation and the anion, the ion pair is termed solvent-shared or solvent separated. This is shown in the diagram below (b)



(b)

Finally, when the ions are in contact with each other, the ion pair is called contact ion pair (c)



(c)

Different ion pairs affect conductivity of electrolyte differently. Generally, the formation of ion pair in an electrolyte will lowers its conductivity.

3.3 Electrochemical interphase

Electrochemistry is concerned with the study of interaction between electrical and chemical effects. This implies that chemical energy can be converted into electrical energy and vice versa. Every electrochemical system must have the electrodes (cathode and anode) and the electrolytes. It has been found that an electrochemical system is not homogenous but heterogeneous systems. Therefore, there exists a certain region call interphase within an electrochemical system.

An electrochemical system can also be defined as a system in which there is a difference of electric potential between two or more phases. The difference in potentials can arise in several ways but the significant ones are

i. Charge transfer between metal-solution interphase
ii. Charge transfer between metal-metal interphase
iii. Charge transfer between solution-solution interphase

Therefore, they are three types of electrochemical interphases, namely, metal-solution interphase, metal-metal interphase and solution-solution interphase. The magnitude of the potential controls the direction and the rate of charge transfer between electrochemical interphase. The study of charge transfer at the interphase is significant because most advantages and applications that can be gotten from electrochemical systems resides or position themselves within the interphase.

3.3.1 Metal-solution interphase: There exist a potential in a metal-solution interphase. For this system, the magnitude and sign of the potential depend on temperature, pressure, the nature of the solvent and the concentration of metal ions in the solution.

Example of electrochemical system where metal-solution interphase potential exists is the K^+/KCl interphase. For example, if a membrane permeable to K^+ ions but not to Cl^- ions separates an aqueous KCl solution from pure water. Diffusion of K^+ ions through the membrane will produce net charges on each phase and generate a potential difference between the phases. Another example is an electrochemical system consisting of a piece of Zn metal dipped into an aqueous solution of $ZnSO_4$ as shown in Fig. 1.13.

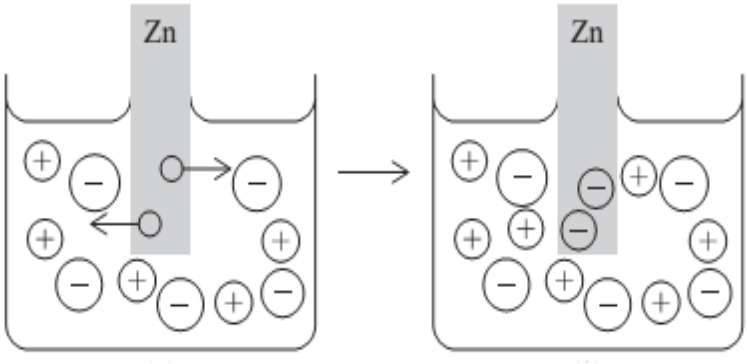


Fig. 1.13: Diagram showing the development of electric potential differences between $Zn_{(s)}$ and $ZnSO_{4(aq)}$

The zinc metal consists of ions and mobile electrons. Its ions can be transferred between the metals and the solution but its electrons cannot enter the solution. Since the zinc metal and the solution contain zinc ions, there are two ways in which the ions can migrate. These include movement of zinc ions from the metal to the solution and the migration from the solution to the zinc metal. If the $ZnSO_4$ solution is extremely dilute. Then the initial rate at which Zn^{2+} ions leave the metal and enter the solution is greater than the rate at which Zn^{2+} ions enter the metal from the solution. This net loss of $Zn^{2+}$from the metal produces a negative charge (excess of electrons)on the Zn electrode, which will slow the rate of the process at which Zn^{2+} ions migrate from the metal to the aqueous solution (equation 7) and increase the rate of the process in which Zn^{2+} ions migrate from the aqueous solution to the metal (equation 8)

$$Zn^{2+}_{(metal)} \rightarrow Zn^{2+}_{(aq)} \qquad 7$$

$$Zn^{2+}_{(aq)} \rightarrow Zn^{2+}_{(metal)} \qquad 8$$

At equilibrium, the rates of these opposing processes are equal and the Gibbs energy *G* of the system is a minimum. Also, at equilibrium, the Zn electrode has a net negative charge, and a potential difference $\Delta\phi$ exists between Zn and the solution.

3.3.2 Metal-metal interphase: In metals, diffusion is very slow, especially at room temperature. Consequently, metal ions do not move at ease between the metal-metal interphase. However, electron moves freely from one metal to another such that at equilibrium, net negative and positive charges are respectively left in each of the metal. A typical example is the interphase that can be created when Cu and Zn metals ate joined together, a net negative charge will be produce on the copper surface while a net positive charge would be produced on the on the Zn metal (Fig. 1.14). The magnitude of the potential difference between the copper and zinc metals will depend on the temperature.

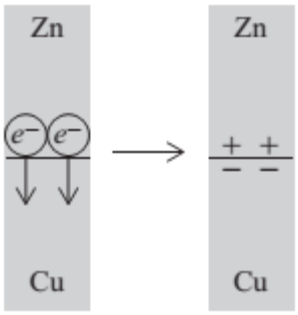


Fig. 1.14: Development of electric potential between $Zn_{(s)}$ and $Cu_{(s)}$

3.3.3 Solution-solution interphase

Although solution-solution interphase is not as common as metal solution interphase, it does exist between two immiscible electrolyte solutions and between two liquid solvents (containing electrolyte) of low mutual miscibility. In most cases, one solvent is usually water while the other maybe a polar organic solvent having a moderate or high dielectric permittivity, (For example, nitrobenzene or 1,2-dichloroethane), that can encourage partial dissociation of dissolved electrolyte(s) into ions. Solution-solution interphase finds wider applications in electroanalysis, phase-transfer catalysis, ion extraction, and electrocatalysis.

In summary, interphase is a boundary condition that cannot be eliminated or avoided in electrochemical systems. Although electrochemical interphases can be a source of obstruction to free flow of ions or materials across the electrodes, its importance cannot be overemphasised. Therefore, the study of the chemistry of interphase is significant. For example, the transfer of charge between two phases, α and β will produce a difference in electric potential between the phases. Let the potentials in the bulk of each of the phases be ϕ^{α} and ϕ^{β} respectively. It can be shown that $\phi^{\alpha} \neq \phi^{\beta}$. The electric potential in the bulk of a phase is called inner potential or the Galvanic potential.

The interphase region between two bulk phases usually contains a complex distribution of electric charge resulting from

i charge transfer between phases,

ii. unequal adsorption of positive and negative ions,

iii. orientation of molecules with permanent dipole moments,

. iv distortion (polarization) of electronic charge in molecules.

Due to the above listed effects, several processes occurring at the interphase must be studied in order to acquire a deeper understanding of an electrochemical interphase. Some of these processes include electric double layer, polarization/over voltage, etc.

4.0 (i) Self Assessment Exercises

1. (a) State three industrial application of electrochemistry

(b) Differentiate between ionic and electrodics

(c) It has been established that conductivity in electrolyte is due to mobility of ions indicating that any factor that affects ion mobility will affects conductivity. Explain the effect of (i) hydration

(ii) Association of water molecule on conductivity of electrolyte.

Use suitable equation and examples to support your answer

2. With the aid of a diagram, highlight the three classes of ion pair that you know

3. Define the term, electrode and state three classes of materials that can be used as an electrode.

4. (a) Highlight the different processes that can create a difference in potential in an electrochemical system.

(b) List the three major electrochemical interphases that you know

(c) What is the factor that control the direction and rate of charge transfer?

(d) Why is the study of electrochemical interphase necessary?

5. What are the factors that are responsible for a complex distribution of charge within the interphase region of an electrochemical system?

6.(a) In every electrochemical system, it is required that there should be an anode and a cathode. If a piece of iron metal is immersed in an aerated water, do you expect to have the anode, cathode and salt bridge in such electrochemical system. Explain.

(b) Write the anodic, cathodic and overall cell reactions for the system. Hence, if the electrode potentials of the cathodic and anodic half reactions are 1.25 and -0.45 V respectively, calculate the cell potential. Hence is the cell reaction spontaneous?

Answers to Self Assessment Exercises

1. (a) Three industrial applications of electrochemistry are

i. The production of sodium, chlorine and aluminium,

ii. electroplating and electrowinning of metals

iii. cathodic and anodic protection of metals against corrosion

(b) Ionics deals with ions in solution and conductivity while electrodics deals with the production of electricity by electrochemical reactions and the production of an electrochemical reactions by an applied electromotive force.

(c) (i) Conductivity in electrolyte is due to mobility of ions. When a salt is dissolved in water, the energy required, is provided by hydration. The extent of hydration depends on the

size and charge of the ion. A small highly charged ion such as K^+ will be easily hydrated than Al^{3+}, which has higher size and charge. Hydrated ions of opposite charge show little tendency to attract ion in aqueous solution because the high permittivity (ε) of water reduces the force (i.e, F) between charges, q_1 and q_2. For two oppositely charge ions with magnitudes, q_1 and q_2, the columbic interaction between them is given as,

$$F = \frac{q_1 q_2}{4\pi l^2 \varepsilon}$$

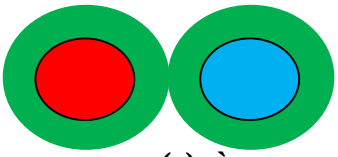
where l is the distant of separation between the charges. ε is the dielectric constant of the solvent. ε= 78.54 for water at 298 K.

Another factor that may affects the conductivity of an electrolyte solution is the association of water molecule with ions (i.e. formation of hydration sheath). This is capable of inhibiting ionic association and can hinder conductivity. For example, at high concentration, Mg^{2+} and SO_4^{2-} associate according to the following equation:

$$Mg^{2+} + SO_4^{2-} = Mg^{2+}SO_4^{2-}$$

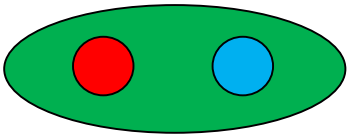
This association can hinder the conductivity of the electrolyte because ions pairs do not conduct electricity

2. Ion pair can be classified as fully solvated, solvent-shared/solvent-separated and contact ion pair. In the Figure below, the solvent is coloured green while the cation and the anion are coloured red and light blue respectively. The diagram represents fully solvated ion pair because both ions (cation and anion) have complete solvation sphere



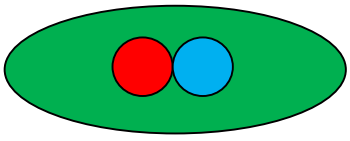
(c) `

However, when there are one solvent molecules between the cation and the anion, the ion pair is termed solvent-shared or solvent separated. This is shown in the diagram below (b)



(b)

Finally, when the ions are in contact with each other, the ion pair is called contact ion pair (c)



(c)

Different ion pairs affect conductivity of electrolyte differently. Generally, the formation of ion pair in an electrolyte will lowers its conductivity.

3. An electrode is an electronic conductor that is in contact with an electrolyte. Electrode materials can be made from metals, semiconductor, graphite or conducting polymers.

4. (a) The three different ways that can cause differences in potentials are

i. Charge transfer between metal solution interphase

ii. Charge transfer between metal-metal interphase

iii. Charge transfer between solution-solution interphase

(b) The three types of electrochemical interphase are

i. metal-solution interphase

ii. metal-metal interphase

iii. solution-solution interphase.

(c) The magnitude of the potential controls the direction and the rate of charge transfer between electrochemical interphase.

(d) The study of charge transfer at the interphase is significant because most advantages and applications that can be gotten from electrochemical systems resides or position themselves within the interphase

5. The interphase region between two bulk phases usually contains a complex distribution of electric charge resulting from

i charge transfer between phases,

ii. unequal adsorption of positive and negative ions,

iii. orientation of molecules with permanent dipole moments,

. iv distortion (polarization) of electronic charge in molecules.

6.(a) The site where oxygen is reduced to water act as the cathode and the site where oxygen is oxidised act as the anode. That means potential differences is created between the oxidation and reduction site. Iron is oxidized to Fe^{2+}(aq) at an anodic site on the surface of the iron, which is often an impurity or a lattice defect. Oxygen is reduced to water at a different site on the surface of the iron, which acts as the cathode. Electrons are transferred from the anode to the cathode through the electrically conductive metal. Water is a solvent for the Fe^{2+} that is produced initially and acts as a salt bridge. Rust ($Fe_2O_3 \bullet xH_2O$) is formed by the subsequent oxidation of Fe^{2+} by atmospheric oxygen.

At the cathode the half-cell reaction (reduction) is

$$O_{2(g)} + 4H^{+}_{(aq)} + 4e^{-} \rightarrow 2H_2O_{(l)} \quad E^0 = 1.23\,V$$

At the anode, the half-cell reaction (oxidation) is

$$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^{-} \qquad E^0 = -0.45$$

The overall cell reaction is obtained by adding the two half-cell reactions as follows

$$Cathodic: \quad O_{2(g)} + 4H^{+}_{(aq)} + 4e^{-} \rightarrow 2H_2O_{(l)} \quad E^0 = 1.23\,V$$

$$\text{Anodic:} \qquad Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^{-} \qquad E^0 = -0.45$$

$$\boldsymbol{Overall: Fe_{(s)} + O_{2(g)} + 4H^{+}_{(aq)} + 2e^{-} \rightarrow Fe^{2+}_{(aq)} + 2H_2O_{(l)}}$$

$$\boldsymbol{E^0_{Cell} = 1.23\,V - (-0.45)V = 1.68\,V}$$

The feasibility of a cell reaction can be estimated through the values of free energy change, which is related to the cell potential through,

$$\boldsymbol{\Delta G^0 = -nFE^0_{Cell} = -2 \times 96500\,C \times 1.68\,V = -324240\ J = -324.24\ J}$$

Since the change in free energy is negative, the cell reaction is spontaneous

(ii) Class Activity

(1) Under what condition is an electrochemical cell reaction spontaneous, non spontaneous and at equilibrium. Provide suitable equations to support your answers (6 marks)

(ii) Differentiate between automobile car battery and touch light (dry cell) (2 marks)

(3) What is the component of tiny electrochemical cell used in hand watch : (2marks)

5.0 Conclusion

Electrochemical cells basically consist of anode, cathode and electrolytes. Within the electrochemical cell, several chemical and physical processes occur at the electrodes, in the bulk solution and in the interphase. Interphase is a boundary condition that cannot be eliminated or avoided in electrochemical systems. Although electrochemical interphases can be a source of obstruction to free flow of ions or materials across the electrodes, its importance cannot be overemphasised. Therefore, the study of the chemistry of interphase is significant.

6.0 Summary

The two types of electrolytic cell are galvanic cells and electrolytic cells. The former converts chemical energy into electrical energy while the later converts electrical to chemical. Electrochemical process is a redox process involving oxidation at the anode and reduction at the cathode.

The transfer of charge between two phases, α and β will produce a difference in electric potential between the phases. The potentials in the bulk of each of the phases, if denoted by ϕ^{α}

and ϕ^{β} respectively, will satisfy the inequality, $\phi^{\alpha} \neq \phi^{\beta}$. The electric potential in the bulk of a phase is called inner potential or the Galvanic potential. The interphase region between two bulk phases usually contains a complex distribution of electric charge resulting from charge transfer between phases, unequal adsorption of positive and negative ions, orientation of molecules with permanent dipole moments and distortion (polarization) of electronic charge in molecules. Therefore, several processes occurring at the interphase must be studied in order to acquire a deeper understanding of an electrochemical system. In this section we shall consider electric double layer, polarization/over voltage and other processes.

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MODULE 1

STUDY UNIT 2: ELECTRIC DOUBLE LAYER

1.0 Introduction

2.0 Intended Learning Outcomes

3.0 Main Content

3.1 Over view of the electric double layer

3.1.1 The double layer models

3.1.2 Application of electric double layer

3.2 Potential at zero charge

4.0 (i) Self Assessment Exercise and Answers

(ii) Class Activity

5.0 Conclusion

6.0 Summary

7.0 References/Further Readings

1.0 Introduction

At any electrode immersed in an electrolyte solution, a specific interfacial region is formed. This region is called the double layer. The electrical properties of such a layer are important, since they significantly affect the electrochemical measurements. In an electrical circuit used to measure the current that flows at a particular working electrode, the double layer can be viewed as a capacitor.

The electric double layer structure and its capacity depend on several parameters such as: electrode material (metals, carbons, semiconductors, electrode porosity, the presence of layers of either oxides or polymeric films or other solid materials at the surface), type of solvent, type of supporting electrolyte, extent of specific adsorption of ions and molecules, and temperature. The composition of the double layer influences the electron transfer rate. Therefore, this section shall consider the concept of the electric double layer, their significant and applications.

2.0 Intended Learning Outcomes

When you have studied this session, you should be able to:

i. introduce the concept of electric double layer
ii. know the three major zones that exist in electrochemical systems
iii. know the different sections in an electric double layer
iv. know and understand the different models behind the electric double layer
v. know the application of electric double layer

vi. understand the concept of potential at zero charge and it's significant.

3.0 Main Content

3.1 Overview of the electric double layer

The application of a potential to an electrochemical cell can caused the surface of the electrode to be charged by specific adsorption of molecules onto its surface. This will lead to the formation of an electric double layer, in which a positive charge is surrounding by a negative charge. Electric double layer is therefore formed by the adsorption of counter ions and the desorption of co-ions at the interphase relative to the concentration in the bulk. Historically, charge distribution in the interphase is called electric double layer because the distribution conforms to every positive ion been surrounded by negative ions and vice versa.

In order to gain more insight into the concept of the electric double layer in an electrochemical cell, we can consider a typical electrochemical compartment to be a universe of three major subset (Fig. 2.1) including,

i. The electrode
ii. The interfacial region (extending from 0.5 to 100 nm)
iii. The bulk solution

At the electrode, Faradic electron transfer occurs on its surface. In the interfacial region, non-Faradic transfer occurs, consequently, ionic concentration differs from that of the bulk solution because of polarization and the production of electric double layer. These changes affect current and cell potential. In the bulk solution, mass transfer from bulk solution to electrode surface occurs. The kinetic of such transfer is governed by diffusion and convection. Therefore, an electric double layer is an interfacial process existing between the electrode and the bulk solution.

A simple demonstration of the double layer process is the interface between a metal electrode and an aqueous electrolyte solution, for example, between Cu and $CuSO_{4(aq)}$. If the electrode is positively charged as a result of net gain of $Cu^{2+}$from the solution, the formation of double layer will ensure that the positively charged electrode is surrounded by negatively charged ions from the solution.

Angel and Reid (2006) modelled the electric double layer phenomenon in terms of the parallel plate capacitor as shown in Fig. 2.2. In the Figure, the positively charged plate of the capacitor is represented by the metal electrode and the negative plate is made of negative ions that are surrounded by their solvation shell. The two types of negative ions that are possible at the interphase are distinguished by the forces that hold them in this region. Specifically, bound ions are those that form a bond with the surface of the electrode (example of specifically

adsorbed ions is Cl^- and Br^-). For specifically bound negative ions, the water molecule in their solvation shell is not as strongly bound compared to positive ions like K^+ and Na^+. The plane that goes through the centred of the specifically adsorbed ion is called inner Helmholtz plane (IHP). The second class of ion that are found outside the electric double layer are the fully solvated ions, which are called non-specifically adsorbed ions and the plane that goes through their centre is called outer Helmholtz plane (OHP). The zone between the OHP and the bulk solution is the diffuse layer.

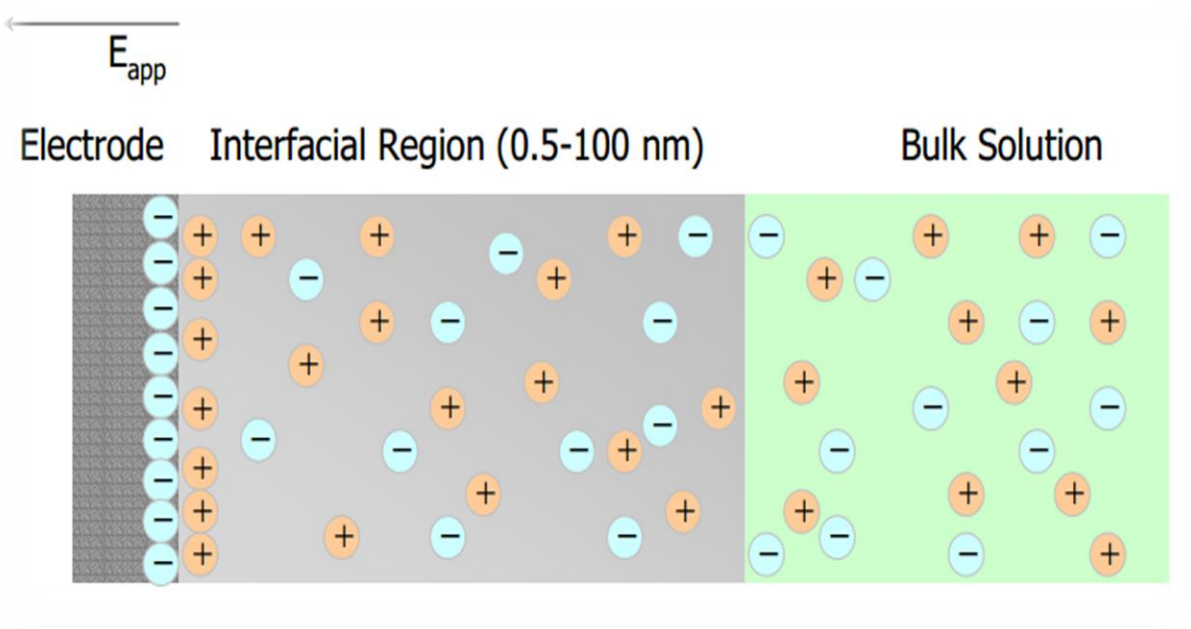

Fig. 2.1: Zones around the electrode

3.1.1 The double layer models

The concept of the existence of the double layer at the surface of a metal that is in contact with an electrolyte started receiving attention in 1879 (Helmholtz). Thus, Helmholtz model (the first theoretical model) assumed the presence of a *compact layer* of ions in contact with the charged metal surface. The next model, Gouy and Chapman, assume a diffuse double layer in which the accumulated ions, due to the Boltzmann distribution, extend to some distance from the solid surface. In further developments, Stern (1924) suggested that the electrified solid-liquid interface includes both the rigid Helmholtz layer and the diffuse one of Gouy and Chapman. However, specific adsorption of ions at the metal surface was pointed out by Graham in 1947. In consecutive developments, the role of the solvent was taken into consideration by Parsons (1954) and Bockris (1963), who suggested that in dipolar solvents, such as water, the dipoles must interact with the charged metal surface. It is also worth noting here that these interactions are promoted by the high concentration of the solvent, which is usually at least several moles

per liter, and about 55.5 M for water. Parsons recognized that the dielectric constant of the solvent in the compact layer of adsorbed molecules is much lower compared to the outer region and approaches the limiting Maxwell value.

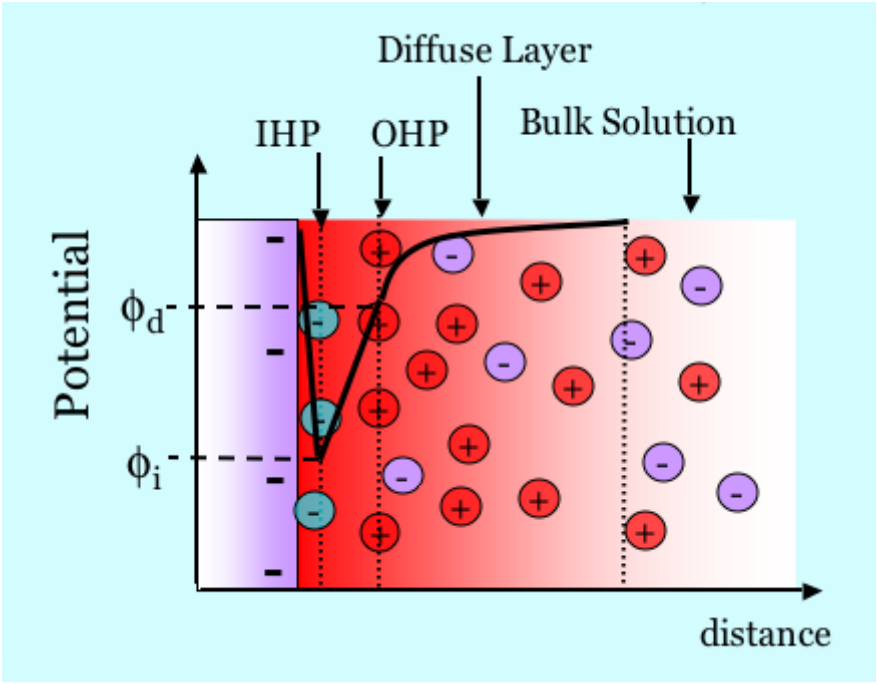

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Fig. 2.2: Diagram showing the different sections in an electric double layer

(Source: https://www.google.com.ng/search?q=electric+double)

3.1.1.1 Stern model and electrode potential

In 1924, Stern proposed that some of the excess negative ions in the solution are adsorbed on the electrode and held at a fixed distance determined by the ionic radius while thermal motion distributes the remainder of the excess negative ions diffusely in the interphase region (Fig. 2.2). Fig. 2.3 shows the variation in the electric potential ϕ with distance from the electrode, as calculated from the Stern model. As we go from phase α to phase β, the electric potential in the interphase region gradually changes fromϕ^{α} to ϕ^{β}. If *z* is the direction perpendicular to the α-β interface, the derivative$\delta\phi\delta z$ is nonzero in the interphase region, which also implies that the electric field, $E_z = - \delta\phi\delta z$ is non zero in the interphase region. An ion or electron with charge *Q* moving from the bulk phase α to the bulk phase β experiences an electric force in the interphase region, its electrical energy changed by $(\phi^{\beta} - \phi^{\alpha})Q$.

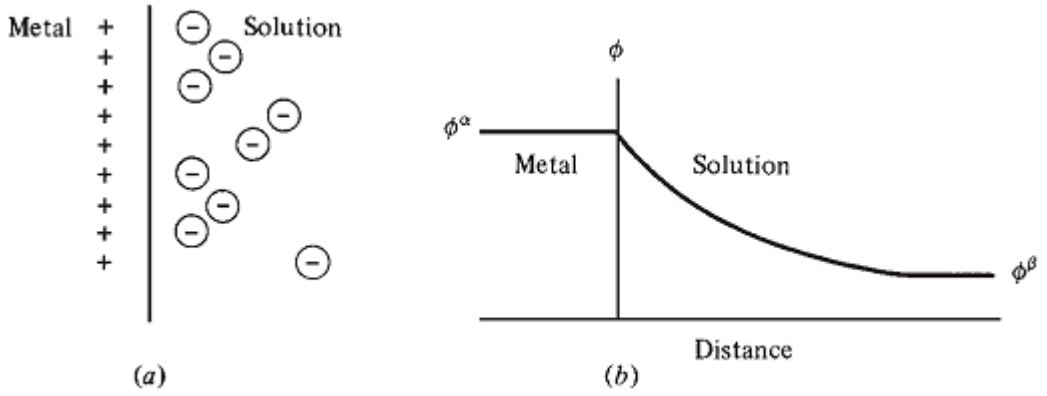

Fig. 2.3: Variation in the electric potential ϕ with distance from the electrode (according to stern model)

3.1.1.2 The classical model

A classic, simplified model of the double layer formed at the metal electrode surface is presented in Fig. 2.4. It is seen in the Figure that a layer of adsorbed water molecules exists on the electrode surface. Since it has been assumed that there is excess of negative charge at the metal phase, the hydrogen atoms of adsorbed water molecules are oriented towards the metal surface. However, it is not a prerequisite that all water molecules at a particular electrode potential and the corresponding excess charge have the same orientation. For excess of positive charge at the metal surface, the dipoles of water will have different orientation. A specifically adsorbed large neutral molecule is also shown in Fig. 2.4. This molecule has removed some water molecules from the surface. On the other hand, a hydrated cation present at the surface has not removed surface water, and therefore cannot be considered as specifically adsorbed. Two planes are usually associated with the double layer. The first one, the inner Helmholtz plane (IHP), passes through the centers of specifically adsorbed ions (compact layer in the Helmholtz model or it is simply located just behind the layer of adsorbed water. The second plane is called the outer Helmholtz plane (OHP) and passes through the centres of the hydrated ions that are in contact with the metal surface. The electric potentials linked to the IHP and OHP are usually written as *Y*2 and *Y*1, respectively. The diffuse layer develops outside the OHP. The concentration of captions in the diffuse layer decreases exponentially with the distance from the electrode surface.

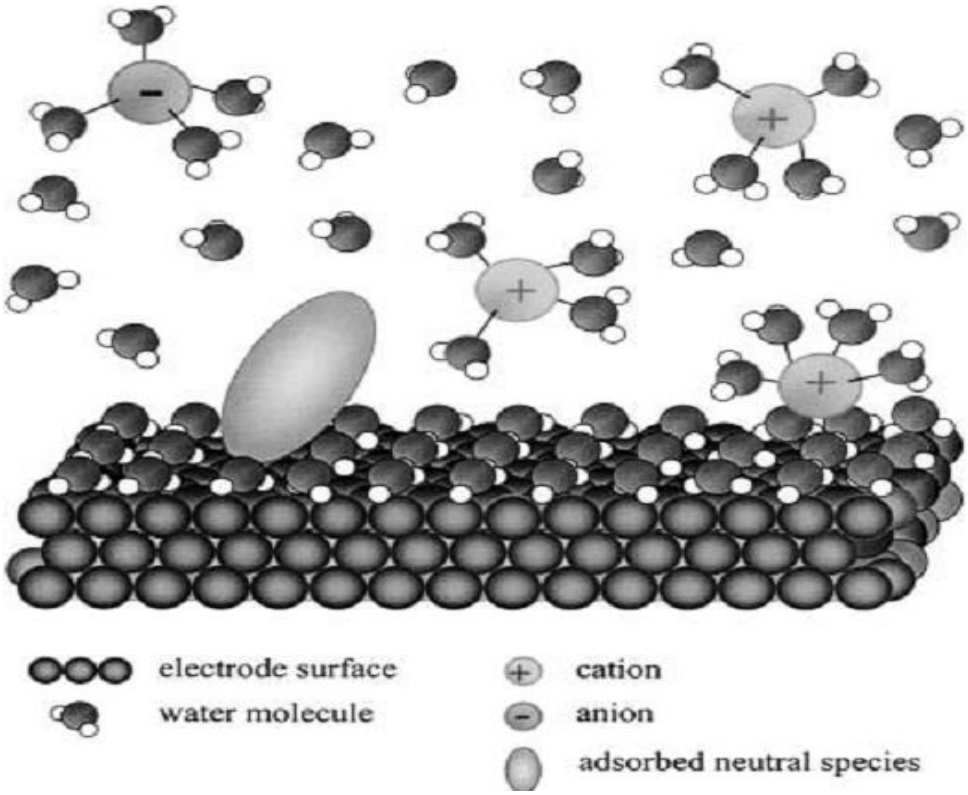

Fig.2.4: General representation of the double layer formed at the metal–electrolyte interface

3.1.1.3 Application of electric double layer

The electric field in the electrode–solution interphase region is extremely high. The falloff in the electrical potential between the metal electrode and the electrolyte solution occurs in a very small distance (approximately 3nm) resulting in an electrical field in the electric double layer as large as 3×10^7 V/cm. Also, the charge that can be accommodated at the surface of the electrode by the specifically and non-specifically adsorbed ions is on the order of 0.1 to 0.2 electron per atom of metal at the surface, the electric double layer has a very large capacitance of 20 to 50 $\mu C/cm^2$. For a typical difference in potential of 1V between the electrode and the solution, the energy stored in the interfacial capacitance can be as large as 150 kJ/kg. Hence electrochemical capacitance can be used to provide backup energy to compensate for power failures in electronic devices.

Worked example 1

(a) Define the different types of electrode potentials that you know and write an equation to show the relationship between them

(b) What are the major sources of the different types of electrode potentials. Hence highlight the major electrochemical interface that you know.

(c) Identify the three major zone in an electrochemical system. Hence highlight the different forms of transfer that is associated with each of the identified zones.

(d) Briefly describe the processes that leads to the formation of electric double layer

(e) What are the factors that affect the structure and capacity of an electric double layer

Solution

(a) The different types of electrode potential are Volta, surface and Galvanic potentials. Volta potential and surface potential. Galvanic potential is also called inner potential and is denoted by the symbol, Φ. Galvanic potential is the work required to move a unit charge from infinity to a given phase. Volta potential or outer potential is denoted by Ψ. It is the electric potential of an electrical charged body, defined as the work required to move a unit electric charge to a distant (approximately a thousand nanometer, outside the phase) that is very close to the phase. Surface potential (χ) is the work required to pass initial charge across the surface layer. Surface potential is majorly contributed by the electric double layer.

The sum of the Volta and surface potential gives the Galvani potential. Therefore, $\Phi = \Psi + \chi$

(b) The difference in potentials can arise in several ways but the significant ones are

iv. Charge transfer between metal-solution interphase

v. Charge transfer between metal-metal interphase

vi. Charge transfer between solution-solution interphase

There are three type of electrochemical interphase, namely,

i. Metal-solution interphase:

ii. Metal-metal interphase:

iii. Solution-solution interphase

(c) A typical electrochemical compartment consists of three major zones including,

iv. The electrode

v. The interfacial region (extending from 0.5 to 100 nm)

vi. The bulk solution

At the electrode, Faradic electron transfer occurs on its surface. In the interfacial region, non-Faradic transfer occurs, consequently, ionic concentration differs from that of the bulk solution because of polarization and the production of electric double layer. These changes affect current and cell potential. In the bulk solution, mass transfer from bulk solution to electrode surface occurs. The kinetic of such transfer is governed by diffusion and convection.

(d) The application of a potential to an electrochemical cell can caused the surface of the electrode to be charged by specific adsorption of molecules onto its surface. This will lead to the formation of an electric double layer, in which a positive charge is surrounding by a

negative charge. Electric double layer is therefore formed by the adsorption of counter ions and the desorption of co-ions at the interphase relative to the concentration in the bulk.

(e) The electric double layer structure and its capacity depend on several parameters such as:

i. electrode material (metals, carbons, semiconductors) and electrode porosity
ii. the presence of oxide layer, polymeric films or other solid materials at the surface
iii. type of solvent
iv. type of supporting electrolyte,
v. extent of specific adsorption of ions and molecules, and temperature.

3.2 Potential at zero charge

In electrochemical systems, the electrode-electrolyte interface is generally charged. If the electrode is polarizable, then its surface charge depends on the electrode potential. IUPAC defines the potential at the point of zero charge as the potential of an electrode (against a defined reference electrode) at which one of the charges defined is zero. The potential of zero charge is used for determination of the absolute potential in a given electrolyte. According to IUPAC, the potential difference with respect to the potential of zero charge can be expressed according to equation 2.1):

$$E_{pzc} = E - E_0 \qquad 2.1$$

where E_{pzc} is the electrode potential difference with respect to the point of zero charge, E is the potential of the same electrode against a defined reference electrode, V, E_0 is the potential of the same electrode when the surface charge is zero, in the absence of specific adsorption other than that of the solvent, against the reference electrode as used above, V

PZC is a characteristic value of the electrode potential for any metal at which a clean surface of the metal will not acquire an electrical charge when it comes into contact with an electrolyte. If the electrode potential is positive in relation to the potential of zero charge, then negative ions are attracted to the metal from the solution; if it is negative in relation to the potential of zero charge, then positive ions are attracted. In both cases, the usual tendency of particles migration from the surface to the bulk phase is repressed because the surface tension at the boundary between the metal and the solution is reduced. With a liquid electrode, for example, a mercury electrode, it is possible to study this effect through electrocapillary curves, which show the relationship between the potential of the metal meniscus in contact with the electrolyte and the extent of capillary rise or fall. At the potential of zero charge, the surface tension is at a maximum, and the electrical capacitance at the boundary is at a minimum. The

potential of zero charge is important in the study of the kinetics of electrode reactions, in the selection of corrosion inhibitors, and in other cases where it is important to consider the adsorption of components on metal surfaces.

In summary, the electric double layer is an electrochemical phenomenon that is worth examining. Although there are minor conflicts between various models aimed at explaining electric double layer, it is certain that the electric double layer problem is an interracial process that extends within a certain distant from the electrode. Detain study on microscopic properties of the double layer will reveal more information. The existence of electric double layer in an electrochemical system connects a vital process because the double layer processes occur within a distant of 0.5 to 100 nm from the electrode. The electric double layer structure and its capacity depend on several parameters such as:

i. electrode material (metals, carbons, semiconductors, electrode porosity,
ii. the presence of layers of either oxides or polymeric films or other solid materials at the surface),
iii. type of solvent,
iv. type of supporting electrolyte,
v. extent of specific adsorption of ions and molecules,
vi. temperature.

Therefore, alteration of any of these functions can alter the nature of the double layer, which may enhance or counter its useful applications.

4.0 (i) Self Assessment Exercises and Answers

1. What are the parameters that affects the structure of an electric double layer?
2. Given an electrochemical cell, identify the three major zones exist between an electrode and electrolyte and explain why the concentration of ions in each of the zone is expected to differ.
3. Differentiate between Faradic charge transfer and non-Faradic charge transfer.
4. In one sentence, briefly describe the Stern model
5. In two sentences, highlight the two planes that are usually found in an electric double layer
6. State one major application of electric double layer
7. Explain the theory for the formation of Helmholtz layer and its limitation

2.8.1 Answers to Self Assessment Questions

1. The electric double layer structure and its capacity are affected by the following factors;

i. electrode material (metals, carbons, semiconductors, electrode porosity,
ii. the presence of layers of either oxides or polymeric films or other solid materials at the surface),
iii. type of solvent, type of supporting electrolyte,
iv. extent of specific adsorption of ions and molecules,
v. temperature. The composition of the double layer influences the electron transfer rate.

2. The three major zones are,
   i. The electrode
   ii. The interfacial region (extending from 0.5 to 100 nm)
   iii. The bulk solution

At the electrode, Faradic electron transfer occurs on its surface. In the interfacial region, non-Faradic transfer occurs, consequently, ionic concentration differs from that of the bulk solution because of polarization and the production of electric double layer.

3. At the electrode, Faradic electron transfer occurs on its surface. In the interfacial region, non-Faradic transfer occurs

4. Stern model states that some of the excess negative ions in the solution are adsorbed on the electrode and held at a fixed distance determined by the ionic radius while thermal motion distributes the remainder of the excess negative ions diffusely in the interphase region

5. Two planes are usually associated with the double layer. The first one, the inner Helmholtz plane (IHP), passes through the centers of specifically adsorbed ions (compact layer in the Helmholtz model), or is simply located just behind the layer of adsorbed water. The second plane is called the outer Helmholtz plane (OHP) and passes through the centres of the hydrated ions that are in contact with the metal surface.

6. Electric double layer provides excellent electrochemical capacitance, which can be used to provide backup energy to compensate for power failures in electronic devices**.**

7. The theory approximate that the surface charge is neutralized by oppositely charged counter ions placed at a distance of *d* from the surface. The surface charge is linearly dissipated from the surface to the counterions satisfying the charge and the distance, *d*, will be to the centre of the counterions (ice the radius). The shortcoming of this model is that it cannot explain all the features of the electric double layer because it assumes rigid layers of opposite charges which is not possible.

(ii) Class Activity

(1) What is the relationship between cell polarization and electric double layer (3 minutes)

(2) What are the shortcoming of Stern, Gua Chaoman and classical models of electric double layer (6 minutes)

5.0 Conclusion

This study section revealed that the electric double layer presents an electrochemical phenomenon that is worth examining. Although there are minor conflicts between various models aimed at explaining electric double layer, it is certain that the electric double layer problem is an interracial process that extends within a certain distant from the electrode. Detain study on microscopic properties of the double layer will reveal more information.

6..0 Summary

The existence of electric double layer in an electrochemical system connects a vital process the presence of charge ions can counter within an electrochemical system. The double layer processes occur within a distant of 0.5 to 100 nm from the electrode. The electric double layer structure and its capacity depend on several parameters such as: electrode material (metals, carbons, semiconductors, electrode porosity, the presence of layers of either oxides or polymeric films or other solid materials at the surface), type of solvent, type of supporting electrolyte, extent of specific adsorption of ions and molecules, and temperature. Therefore, altering any of this function can alter the nature of the double layer, which may enhance or counter its useful applications.

The importance of the EDL has led to numerous studies, and many models were proposed in the past. The best known is the Gouy–Chapman model, in which ions are considered as point charges and water is considered as a continuum.

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Link to slide show:https://www.slideshare.net/GamryInstruments/echem-basics-for-users

MODULE 2

STUDY UNIT 1: POLARIZATION AT INTERPHASE

1.0 Introduction

2.0 Intended Learning Outcomes

3.0 Main Content

3.1 Polarization at the interface

3.1.1 Polarizable and non polarizable interphases

3.1.2 Polarization of a single electrode

3,2 Dependent of activation overpotential on current

3,2 The Nernst equation

4.0 (i) Self Assessment Exercise and Answers

(ii) Class Activity

5.0 Conclusion

6.0 Summary

7.0 References/Further Readings

1.0 Introduction

When a small current or potential is applied to an electrochemical system, the response is in many cases linear. The effective resistance can, however, vary over a wide range. When this resistance is high, we have a polarizable interface, meaning that a small current generates a high potential across it (i.e., the interface is polarized to a large extent). When the effective resistance is low, the interface is said to be non polarizable.
In this case a significant current can be passed with only minimal change in the potential.

The concept of the ideal polarizability was first introduced by F. O. Koenig in 1934. Ideally polarizable electrode (also ideal polarizable electrode or ideally polarized electrode), in electrochemistry is an electrode that is characterized by an absence of net current between the two sides of the electric double layer, i.e., no faradic current between the electrode surface and the electrolyte. Any transient current that may be flowing is considered non-faradic but in non-polarizable electrode, a faradic current can freely pass (without polarization).

The classical examples of the two ideal types of electrodes, polarizable and non-polarizable, are the platinum and the silver/silver chloride electrodes, respectively.

2.0 Intended Learning Outcomes

When you have studied this session, you should be able to:

i. Understand the concept of polarization in electrochemistry

ii. Know the different types of polarization and overpotentials
iii. Understand the nature of plots expected for cathodic and anodic polarizations
iv. Explain polarization of a single electrode
v. Derive Tafel equation for polarization
vi. Plots potentiodynamic polarization plot and calculate Tafel constants from the plot

3.0 Main Content

3.1 Polarization at the interface

3.1.1 Polarizable and non-polarizable Interfaces

A non polarizable electrode is, in effect, a reversible electrode. A good reference electrode is always a reversible electrode. The inverse is not necessarily true. Not every reversible electrode is suitable as a reference electrode. For example, the correct thermodynamic reversible potential of a metal/metal-ion electrode may be hard to reproduce, because of impurities in the metal or complexing agents in the solution, even when the interface is highly non polarizable. Polarizable interfaces behave differently. Their potential is not fixed by the solution composition, and it can be changed at will over a certain range, depending on the metal and the composition of the solution in contact with it. For such a system the potential may be viewed as an additional degree of freedom in the thermodynamic sense, as used in the Gibbs phase rule.

To be sure, a so-called non polarizable interface can be polarized by passing a significant current through it. This, however, alters the concentration of both the reactant and the product at the electrode surface (without changing significantly their bulk concentrations). The potential developed across the interface will be in agreement with the Nernst equation, as long as the concentrations used are the surface concentrations, which depend on the current passing across the interface.

In order to further gain insight knowledge into the concept of polarization, let us see what happened to current in an electrochemical cell at equilibrium. In doing this, we write an equilibrium cell equation for the cell given in Fig. 3.1 as follows,

$$M^{n+} = M + ne^{-} \qquad 3.1$$

The current flow can be divided into cathodic and anodic current (i.e., I_A and I_C) and at equilibrium, $I_A = I_C = I_0$. I_0 is called exchange current density. I_0 has been found to depend on the surface of the electrode. For example, for the electrochemical system defined as $2H^+ + 2e^- = H_2$, experimental value of I_O is found to be 10^{-12} and 10^{-3} Acm^2 on mercury and platinum electrode respectively.

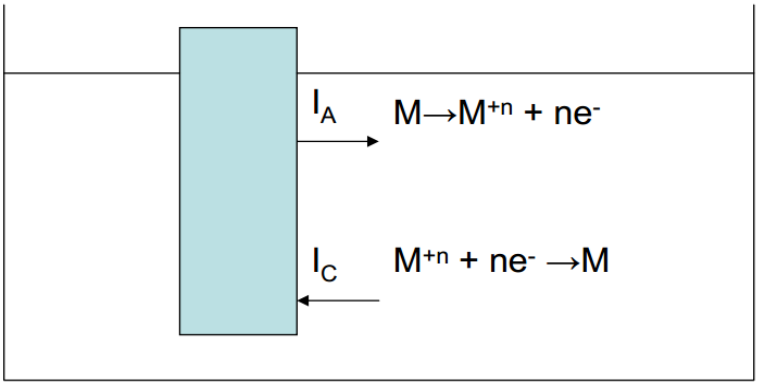

Fig. 3.1: Diagram showing reactions in a single electrochemical electrode

3.1.2 Polarization of a single electrode

Consider equation 3.1, if we disturb the equilibrium by pumping current to the system, the equilibrium will proceed faster in the cathodic reaction direction (equation 11) and the potential will become more negative (see Fig. 3.2). In this case, $I_C >>> I_A$ and the plot of E versus I slopes downward

$$M^{n+} + ne^- \rightarrow M \qquad 3.2$$

On the other hand, if we take away current from the equilibrium reaction (equation 3), the reaction will proceed faster in anodic direction and the potential will become more positive (equation 5). In this case, $I_A >>> I_B$ (see Fig. 3.3)

$$M \rightarrow M^{n+} + ne^- \qquad 3.3$$

In Figs. 3.2 and 3.3, E denotes the electrode potential while e stands for the equilibrium potential. The change in electrode potential (E) from the equilibrium potential is called polarization. The difference between E and e is called overvoltage that is,

$$\eta = E(i) - e \qquad 3.4$$

For cathodic polarization, E< e and η_C is negative (equation 3.5) but for anodic polarization, E > e and η_A is positive

$$\eta_C = E(i) - e \qquad 3.5$$

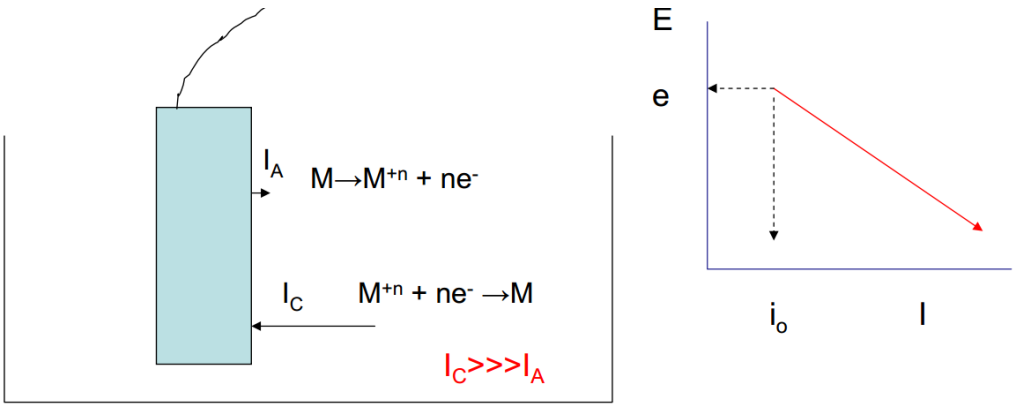

Fig. 3.2: Diagram showing anodic polarization in a single electrode system

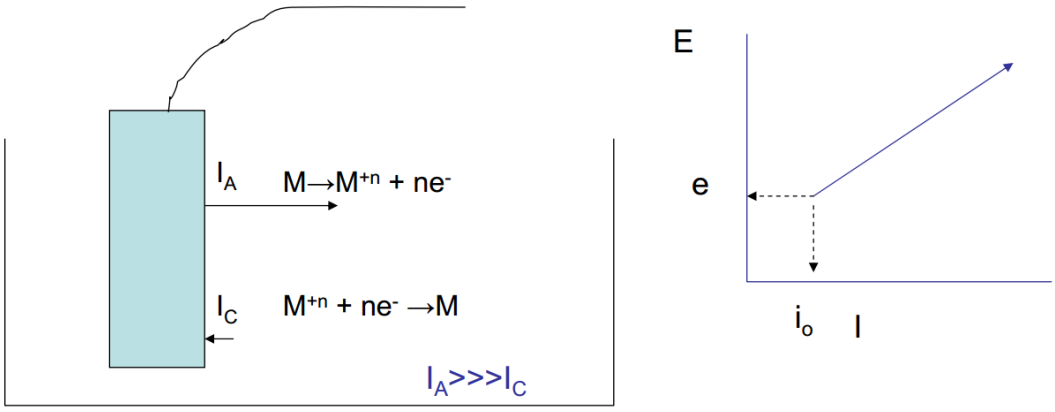

Fig. 3.3: Diagram showing cathodic polarization in a single electrode system

We have just discussed polarization of a single electrode. However, a typical electrochemical cell consists of two electrodes (anode and cathode), indicating that combine effect of anodic and cathodic polarizations must be examined. Generally, there are two types of polarization in an electrochemical cell, namely, concentration (η_C) and activation polarization (η_{act}). Activation polarization is caused by charge transfer across the electrode/electrolyte interface while concentration polarization is caused by changes in the concentration of the ions near the electrode/electrolyte interface. The sum of η_C and η_{act} gives the total polarization across the electrode, thus,

$$\eta = \eta_C + \eta_{act} \qquad 3.6$$

3.2 Dependent of activation overpotential on current: Tafel law

In 1905, Tafel (1862-1981) found that for most electrode reaction, the overpotential (η_{act}) is linearly proportional with the log of the current as follows,

$$\eta_{act} = \beta \log(i_o) + \beta log(i) = \beta log\left(\frac{i}{i_o}\right) \qquad 3.7$$

For anodic and cathodic polarizations, equation 16 can be simplified to equations 3.8 and 3.9 respectively,

$$\eta_{act,a} = \beta_a \log(i_o) + \beta_a log(i_a) = \beta_a log\left(\frac{i_a}{i_o}\right) \quad 3.8$$

$$\eta_{act,c} = \beta_c \log(i_o) + \beta_c log(i_c) = \beta_c log\left(\frac{i_c}{i_o}\right) \quad 3.9$$

β_a and β_c are called Tafel constants. Generally, $\beta = \frac{2.3RT}{\propto nF}$, where α≈ 0.5.

Most often, activation polarization is normally studied by using electrochemical instrument that is able to generate data for the variation of electrode potential with current. Results obtained from such studies are normally treated graphically. A typical plot of this nature (for the reaction, $M^{n+} + ne^- = M$) is shown in Fig. 3.4. It can be seen from Fig.22 that Tafel constants can be obtained from the slopes of the cathodic and anodic arms of the plot. A plot of this nature is called potentiodynamic polarization plot. Specific example of potentiodynamic polarization curve for the system, $2H^+ + 2e^- = H_2$, is presented in Fig. 23. For this reaction at equilibrium, no current flows and the reaction potential is 0 V but at standard condition, i_o = 1 mA/cm^2. If current is allowed to flow, the potential E, changes and the overpotential can be calculated, using Tafel equation (equation 3.10), thus

$$\eta_{act,a} = \beta_a log\left(\frac{i_a}{i_o}\right) = 0.1log\left(\frac{10}{1}\right) = 0.1\ V \quad 3.10$$

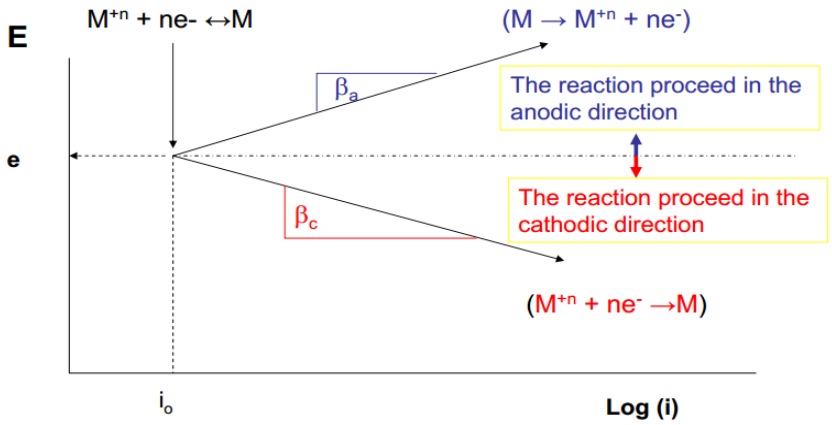

Fig. 3.4: Typical pattern of plot for the variation of E with log(i)

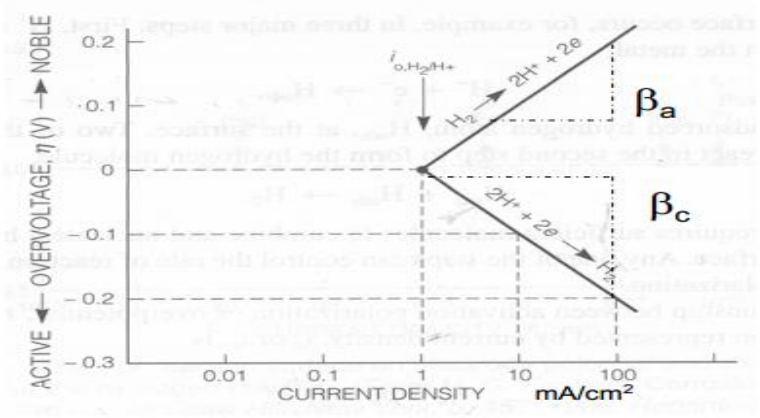

Fig. 3.5: Plot of E versus log(i) for the reaction, $2H^+ + 2e^- = H_2$

Worked example 1

(a) Use suitable equations or notations to explain what is exchange current density

(b) With reference to a polarography cell, discuss the effect of temperature coefficient of the half wave on reversible and irreversible reaction

(c) Explain what is reversible and irreversible electrode reactions

Solution

(a) Exchange current density, i_0 is the equilibrium current obtained when the anodic and cathodic current are equal. i.e., at equilibrium (dynamic equilibrium), $i_0 = i_c = i_a$.

Under this condition, no net current flows across the electrodes but both reduction and oxidation take place at equal rate, so that the composition of the electrolyte does not change.

(b) The temperature coefficient of the half-wave potential is mostly between –2 and +2 mv/degree.

For a reversible wave it may be either positive or negative.

For an irreversible wave it is usually positive and may exceed several millivolts per degree.

(c) The reversible reactions are so rapid that thermodynamic equilibrium is very nearly attained at every instant during the life of a drop at any potential. For such reactions the variation of current with potential reflects the changing position of the equilibrium and is described by Nernst equation.

Irreversible electrode reactions are so slow that they proceed only by a fraction of the way towards equilibrium during the life of each drop. For these reactions it is the rate of the electron-

transfer process and the manner in which this is influenced by the electrode potential that governs the relationship between current and potential.

Worked example 2

(a) Differentiate between polarizable and non polarizable interphases

(b) Consider the following chemical reaction and answer the questions that follows it,

+ $$M^{n+} = M + ne^-$$

(i) What will happen the change in electrode potential if current is pumped or withdrawn from the electrode system? Sketch suitable graphs to support your answer

(ii) What is the meaning of exchange current density?

(c) What is the relationship between electrode potential and overpotential?

(d) Differentiate between the two types of polarization that you know and provide suitable equation to show how they are related.

Solution

(a) A polarizable interface is an interface that generates a high potential across it (i.e., the interface is polarized to a large extent) when a small current is applied, especially when the resistance is high. However, when the effective resistance is low, the interface is said to be non polarisable because the passage of a significant current will result in only a minimal change in the potential.

(b)(i) Consider the equation, if we disturb the equilibrium by pumping current to the system, the equilibrium will proceed faster in the cathodic reaction direction (see equation below) and the potential will become more negative (see Fig. 3.6a). In this case, $I_C >>> I_A$ and the plot of E versus I slopes downward, i. e

$$M^{n+} + ne^- \rightarrow M$$

On the other hand, if we take away current from the equilibrium reaction, the reaction will proceed faster in anodic direction and the potential will become more positive (see equation below). In this case, $I_A >>> I_B$ (see Fig. 3.6b):

$$M \rightarrow M^{n+} + ne^-$$

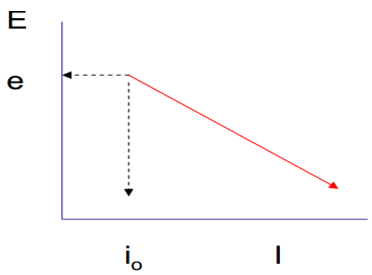

Fig. 3.6a: Anodic polarization in a single electrode system

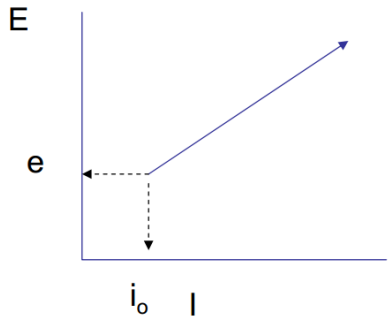

Fig. 3.6b: Cathodic polarization in a single electrode system

In Figs. 3.6a and 3.6b, E denotes the electrode potential while e stands for the equilibrium potential. The change in electrode potential (E) from the equilibrium potential is called polarization. The difference between E and e is called overvoltage that is,

$$\eta = E(i) - e$$

For cathodic polarization, E< e and η_C is negative (see equation below) but for anodic polarization, E > e and η_A is positive

$$\eta_C = E(i) - e$$

(c) The difference between E and e is called overvoltage that is,

$$\eta = E(i) - e$$

For cathodic polarization, E< e and η_C is negative but for anodic polarization, E > e and η_A is positive

$$\eta_C = E(i) - e$$

(d) Generally, there are two types of polarization in an electrochemical cell, namely, concentration (η_{Con}) and activation polarization (η_{act}). Activation polarization is caused by charge transfer across the electrode/electrolyte interface while concentration polarization is caused by changes in the ion's concentration near the electrode/electrolyte interface. The sum of η_{Con} and η_{act} gives the total polarization across the electrode, thus,

$$\eta = \eta_{Con} + \eta_{act}$$

Worked example 3

(a) Write the Tafel equation for anodic, cathodic and overall polarizations and explain how the Tafel constants can be obtained from a polarization plot.

(b) From first principle, show that the Nernst equation can be written as $E = E^0 - (25.67\ mV)lnQ$

(c) Show that for the Daniel cell, the Nernst equation can be written as, $E_{cell} = E^0_{cell} - \frac{0.059}{2} log\left(\frac{[Zn^{2+}]}{[Cu^{2+}]}\right)$

Solution

(a)

In 1905, Tafel (1862-1981) found that for most electrode reactions, the overpotential (η_{act}) is proportional to the logarithm of the current, according to the following equation

$$\eta_{act} = \beta \log(i_o) + \beta log(i) = \beta log\left(\frac{i}{i_o}\right) \quad \text{(i)}$$

For anodic and cathodic polarizations, equation 1 can be simplified to equations 2 and 3 respectively,

$$\eta_{act,a} = \beta_a \log(i_o) + \beta_a log(i_a) = \beta_a log\left(\frac{i_a}{i_o}\right) \quad \text{(ii)}$$

$$\eta_{act,c} = \beta_c \log(i_o) + \beta_c log(i_c) = \beta_c log\left(\frac{i_c}{i_o}\right) \quad \text{(iii)}$$

The Tafel constants, $\beta_a \; and \; \beta_C$ can be obtained from the slopes of the anodic and cathodic polarization plots respectively.

(b) For a typical electrochemical reaction, the change in standard change in free energy is related to the reaction quotient, according to equation i,

$$\Delta G = \Delta G^0 + RTlnQ \quad \text{(i)}$$

However, the relationship between the change in free energy and the electromotive force is given as, $\Delta G = -nFE$, which when substituted to equation i, yields equation (ii),

$$-nFE = -nFE^0 + RTlnQ \quad \text{(ii)}$$

Dividing equation ii by –nF leads to equation iii,

$$E = E^0 - \frac{RT}{nF} lnQ \quad \text{(iii)}$$

Equation iii is the Nernst equation, which reveals that the cell potential relates linearly with the reaction quotient, Q. The standard emf, i.e. E^0 is the electrode potential when all the reactants and products are in their standard state. That means, when Q = 1, indicating that lnQ = 0. E^0 is strongly related to ΔG^0. At 25 ° C (i.e. 298 K), the ratio, RT/F is equal to 0.025678 V = 25.67 mV. This means that for one mole (n = 1), the Nernst equation can be re-written as,

$$E = E^0 - (25.67\, mV) lnQ$$

(c) The cell reactions for the Daniel cell are,

$$Anodic\ half\ reaction\ (oxidation): Zn_{(s)} = Zn^{2+}_{(aq)} + 2e^-$$

$$Cathodic\ half\ reaction\ (reduction): Cu^{2+}_{(aq)} + 2e^- = Cu_{(s)}$$

$$\boldsymbol{Overall\ reaction: \; Zn_{(s)} + Cu^{2+}_{(aq)} = Zn^{2+}_{(aq)} + Cu_{(s)}}$$

Application of the Nernst equation leads to the following equations,

At the cathode,

$$E_{Cu^{2+}/Cu} = E^0_{Cu^{2+}/Cu} - \frac{RT}{2F} ln\left(\frac{1}{[Cu^{2+}]}\right)$$

At the anode, the electrode potential is given as,

$$E_{Zn^{2+}/Zn} = E^0_{Zn^{2+}/Zn} - \frac{RT}{2F} ln\left(\frac{1}{[Zn^{2+}]}\right)$$

The cell potential will be given as,

$$E_{cell} = E_{Cu^{2+}/Cu} - E_{Zn^{2+}/Zn}$$

$$E_{cell} = \left(E^0_{Cu^{2+}/Cu} - E^0_{Zn^{2+}/Zn}\right) - \frac{RT}{2F} ln\left(\frac{1}{[Cu^{2+}]}\right) - \frac{RT}{2F} ln\left(\frac{1}{[Zn^{2+}]}\right)$$

$$E_{cell} = \left(E^0_{Cu^{2+}/Cu} - E^0_{Zn^{2+}/Zn}\right) - \frac{RT}{2F}\left\{ln\left(\frac{1}{[Cu^{2+}]}\right) - ln\left(\frac{1}{[Zn^{2+}]}\right)\right\}$$

$$E_{cell} = E^0_{cell} - \frac{RT}{2F} ln\left(\frac{[Zn^{2+}]}{[Cu^{2+}]}\right)$$

$$E_{cell} = E^0_{cell} - \frac{0.059}{2} log\left(\frac{[Zn^{2+}]}{[Cu^{2+}]}\right)$$

Worked example 4

(a) Write an equation to show the relationship between the two types of polarization and total polarization

(b) Write and expression for cathodic polarization and anodic polarization. Hence calculate the cathodic and anodic polarization when the electrode potential at equilibrium is 12 V and the shifts in potentials are 6 and 32 V respectively.

Solution

(a) The sum of η_{Con} and η_{act} gives the total polarization across the electrode.

$$\eta = \eta_{Con} + \eta_{act}$$

(b) Cathodic polarization (overvoltage) is given as, $\eta_C = E(i) - e$. Where e is the equilibrium electrode potential and E is the potential generated by the cathodic reaction.

For anodic polarization (overvoltage), $\eta_a = E(i) - e$.

Calculations, Given

Cathodic polarization is positive

e = 12 mV

E = 6 mV

$\eta_C = E(i) - e$

$= (6 - 12)mV = -6\,mV$

For anodic, the shift is positive

e = 12 mV

E = 24 mV

$\eta_a = E(i) - e = (32 - 12)mV = 20\,mV$

3.3 The Nernst equation

The Nernst equation is used to determine the equilibrium reduction potential of a half cell in an electrochemical cell. It can also be used to determine the full voltage of a complete electrochemical cell. Cell potential is the potential difference between the two electrodes in the cell. It is measured in volt. Cell potential is a significant function because it determines the amount of work that can be done by the cell. The higher the potential, the greater the work the cell can overcome. The maximum work a cell can do is given by ΔG. Therefore, for a spontaneous work at constant pressure and temperature, ΔG is equal to the maximum work done by the cell under reversible condition and at specified composition. For a typical electrochemical reaction, the change in free energy is related to the reaction quotient, according to equation 3.11,

$$\Delta G = \Delta G^0 + RTlnQ \qquad 3.11$$

However, the relationship between the change in free energy and the electromotive force is given as, $\Delta G = -nFE$, which when substituted to equation 3.11, yields equation 3.12,

$$-nFE = -nFE^0 + RTlnQ \qquad 3.12$$

Dividing equation 21 by –nF leads to equation 3.13,

$$E = E^0 - \frac{RT}{nF}lnQ \qquad 3.13$$

Equation 3.13 is the Nernst equation, which reveals that the cell potential relates linearly with the reaction quotient, Q. The standard emf, i.e. E^0 is the electrode potential when all the reactants and products are in their standard state. That means, when Q = 1, indicating that lnQ = 0. E^0 is strongly related to ΔG^0. At 25 ° C (i.e. 298 K), the ratio, RT/F is equal to 0.025678 V = 25.67 mV. This means that for one mole (n = 1), the Nernst equation can be re-written as,

$$E = E^0 - (25.67\,mV)lnQ$$

Consider an increase in the value of Q by a factor of 10, then, $E = E^0 - (25.67\,mV)\ln(10)$ or $E = E^0 - 59.18$, which implies that the cell potential decreases by a factor of 59.18. On the otherhand, if Q is decreased by a factor of 10, the emf becomes, $E =$

$E^0 - (25.67\ mV)\ln(0.1)$ or $E = E^0 + 59.18$, hence the cell potential becomes more positive by a factor of 59.18.

The Nernst equation for a concentration cell such as, $M|M^+(aq,R)\|M^+(aq,L)|M$ can be written as,

$$E = -\frac{RT}{nF} ln\left(\frac{a_L}{a_R}\right) \qquad 3.14$$

where a_L and a_R are the activities of the specie in the left and right respectively. In this case, $E^0 = 0$.

For a general redox reaction, $Oxid + e^- = Red$, the Nernst equation can be written as,

$$E = E^0 - \frac{RT}{nF} ln\left(\frac{[Reduced]}{[Oxidized]}\right) \qquad 3.15$$

Given an redox equation such as, $M^{n+}_{(aq)} + ne^- \rightarrow M_{(s)}$, the electrode potential at any concentration, measured with respect to standard hydrogen electrode (SHE) can be represented as,

$$E_{M^{n+}/M} = E^0_{M^{n+}/M} - \frac{RT}{nF} ln\left(\frac{[M]}{[M^{n+}]}\right)$$

Since M is a solid, its activity is taken to be unity, hence the equation becomes,

$$E_{M^{n+}/M} = E^0_{M^{n+}/M} - \frac{RT}{nF} ln\left(\frac{1}{[M^{n+}]}\right)$$

Consider the Daniel cell, which is an electrochemical cell operating with various concentrations of Cu and Zn ions. At the cathode, the electrode potential is given as,

$$E_{Cu^{2+}/Cu} = E^0_{Cu^{2+}/Cu} - \frac{RT}{2F} ln\left(\frac{1}{[Cu^{2+}]}\right)$$

At the anode, the electrode potential is given as,

$$E_{Zn^{2+}/Zn} = E^0_{Zn^{2+}/Zn} - \frac{RT}{2F} ln\left(\frac{1}{[Zn^{2+}]}\right)$$

The cell potential will be given as,

$$E_{cell} = E_{Cu^{2+}/Cu} - E_{Zn^{2+}/Zn}$$

$$E_{cell} = \left(E^0_{Cu^{2+}/Cu} - E^0_{Zn^{2+}/Zn}\right) - \frac{RT}{2F} ln\left(\frac{1}{[Cu^{2+}]}\right) - \frac{RT}{2F} ln\left(\frac{1}{[Zn^{2+}]}\right)$$

$$E_{cell} = \left(E^0_{Cu^{2+}/Cu} - E^0_{Zn^{2+}/Zn}\right) - \frac{RT}{2F}\left\{ln\left(\frac{1}{[Cu^{2+}]}\right) - ln\left(\frac{1}{[Zn^{2+}]}\right)\right\}$$

$$E_{cell} = E^0_{cell} - \frac{RT}{2F} ln\left(\frac{[Zn^{2+}]}{[Cu^{2+}]}\right)$$

$$E_{cell} = E^0_{cell} - \frac{0.059}{2} log\left(\frac{[Zn^{2+}]}{[Cu^{2+}]}\right)$$

From the above, it can be seen that the cell potential increases with increase in the concentration of Cu^{2+}ion. For a general electrochemical reaction of the type,

$$aA + bB = cC + dD$$

The Nernst equation can be written as,

$$E_{cell} = E^0_{cell} - \frac{RT}{nF} ln\left(\frac{[C]^c[D]^d}{[A]^a[B]^b}\right)$$

Worked example 5

Given that the standard electrode potential of the Daniel cell is 1.1 V at 298 K. Explain how the cell reaches equilibrium within a given time of usage, hence calculate the equilibrium constant of the cell.

(a) Also calculate the free energy change of the cell

Solution

The cell reaction for the Daniel cell can be written as,

$$Cu^{2+}_{(aq)} + Zn_{(aq)} \rightarrow Cu_{(aq)} + Zn^{2+}_{(aq)}$$

From the Nernst equation, the electrode potential of the Daniel cell can be written as,

$$E_{cell} = E^0_{cell} - \frac{RT}{2F} ln\left(\frac{[Zn^{2+}]}{[Cu^{+}]}\right)$$

When the cell is running with time, the concentration of Cu^{2+} will be decreasing while the concentration of Zn^{2+} will be increasing. This will continue to drop the electrode potential of the cell until it reaches equilibrium, where there is no further change in concentration. At equilibrium, $E_{cell} = 0$ and the standard electrode potential of the cell becomes,

$$0 = E^0_{cell} - \frac{RT}{2F} ln\left(\frac{[Zn^{2+}]}{[Cu^{+}]}\right)$$

$$E^0_{cell} = \frac{RT}{2F} lnK_C$$

Given that $E^0_{cell} = 1.10\ V$, then

$$lnK_C = \frac{2FE^0_{cell}}{RT} \frac{2(96489\ C)(1.1V)}{(8.314 J/mol/K)(298\ K)} = 85.679$$

$$K_C = 3.24 \times 10^{37}$$

(b) The free energy change of the cell is related to the equilibrium constant, i.e.

$$\Delta G = -RTlnK_C = -\left(\frac{8.314\frac{J}{mol}}{K}\right)(298\ K)(85.679) = -212.275\ kJ/mol$$

Worked example 6

Calculate the equilibrium constant and free energy change of the cell given below, if at 298 K, $E^0_{cell} = 0.46\ V$

$$Cu_{(s)} + Ag^{+}_{(aq)} \rightarrow Cu^{2+}_{(aq)} + Ag_{(s)}$$

Solution

At equilibrium, the E_{cell} =0 and the Nernst equation for the given cell becomes,

$$0 = E^0_{cell} - \frac{RT}{2F} ln\left(\frac{[Cu^{2+}]}{[Ag^{+}]}\right)$$

$$E^0_{cell} - \frac{RT}{2F} lnK_C$$

$$. lnK_C = \frac{2FE^0_{cell}}{RT} \frac{2(96489\ C)(0.46V)}{(8.314 J/mol/K)(298\ K)} = 35.8294$$

$$K_C = 3.635 \times 10^{15}$$

The free energy change is given as

$$\Delta G = -RTlnK_C = -(8.314\ kJ/mol/K)(298\ K)(35.8294) = -88.77\ kJ/mol$$

Worked example 7

(a) Given an electrochemical reaction, represented as, $Oxid + e^- = Red$, where Oxid is the oxidised specie and Red is the reduced specie present at equilibrium The concentration of Oxid and Red are C_o and C_R respectively and they are very low. Answer the following questions,

(i) Show that at equilibrium, $ln\left(\frac{C_O\ (0,t)}{C_R\ (0,t)}\right) = ln\left(\frac{k_{a,0}}{k_{c,0}}\right) = \frac{\Delta G^*_c - \Delta G^*_a}{RT}$

(ii) Apply the Nernst equation to the expression in (i) above and derive the Butler-Volmer equation

(iii) Consider the derived Butler-Volmer equation. If the over potential is extremely negative or positive, show that the resulting equations will be equivalent to cathodic and anodic Tafel plots, that can be useful in estimating useful quantities.

Solution

(i) The rate of cathodic (R_C) and anodic (R_a) reactions can be written as follows,

$$R_c = k_c C_O\ (0.t)$$
$$R_a = k_a C_R\ (0.t)$$

The net rate is the difference, i.e., $R_{net} = R_c - R_a$, therefore,

$$R_{net} = k_c C_O(0.t) - k_a C_R\ (0.t)$$

The cathodic and anodic rate constants vary with temperature according to the following equation,

$$k_c = exp\left(\frac{-\Delta G^*_c}{RT}\right)$$
$$k_a = exp\left(\frac{-\Delta G^*_a}{RT}\right)$$

At equilibrium, $R_a = R_c$ and $k_c C_O(0.t) = k_a C_R\ (0.t)$. The equilibrium constant can be defined as the ratio of R_a to that of R_c. Therefore,

$$\frac{k_a}{k_c} = \frac{C_O\,(0,t)}{C_R\,(0,t)} = \frac{exp\left(\frac{-\Delta G_a^*}{RT}\right)}{exp\left(\frac{-\Delta G_c^*}{RT}\right)} = exp\left(\frac{-\Delta G_a^*}{RT} + \frac{\Delta G_c^*}{RT}\right) = exp\left(\frac{\Delta G_c^*}{RT} - \frac{\Delta G_a^*}{RT}\right)$$

Simplification of equation 31 yields equation 32

$$ln\left(\frac{C_O\,(0,t)}{C_R\,(0,t)}\right) = ln\left(\frac{k_{a,0}}{k_{c,0}}\right) = \frac{\Delta G_c^* - \Delta G_a^*}{RT}$$

(ii) Application of the Nernst equation to the above equilibrium process leads to equation 33,

$$E_e = E^0 + \frac{RT}{F} ln\left(\frac{C_0}{C_R}\right) \qquad 1$$

$$ln\left(\frac{C_0}{C_R}\right) = \frac{F}{RT}(E_e - E^0) \qquad 2$$

Since $ln\left(\frac{C_0}{C_R}\right) = \frac{\Delta G_c^* - \Delta G_a^*}{RT}$, The above equation becomes,

$$\frac{\Delta G_c^* - \Delta G_a^*}{RT} = \frac{F}{RT}(E_e - E^0) \qquad 3$$

$$\Delta G_c^* - \Delta G_a^* = F(E_e - E^0) \qquad 4$$

Equation 4 can be separated for the cathodic and for the anodic reactions by introducing a symmetry factor called the transfer coefficient, α and β respectively. α is the transfer coefficient for the cathode and β is the transfer coefficient for the anode. β = 1- α. Therefore, α + β = 1 and the following equations are hereby obtained,

$$\Delta G_c^* = \Delta G_0^* + \alpha F(E_e - E^0) \qquad 5$$

$$\Delta G_a^* = \Delta G_0^* - \beta F(E_e - E^0) \qquad 6$$

Since $k_c = exp\left(\frac{-\Delta G_c^*}{RT}\right)$ and $k_a = exp\left(\frac{-\Delta G_a^*}{RT}\right)$, then

$$k_{c,0} = exp\left(\frac{-\Delta G_0^*}{RT}\right) exp\left(\frac{-\alpha F(E_e - E^0)}{RT}\right) \qquad 7a$$

$$k_{c,0} = k_0\, exp\left(\frac{-\alpha F(E_e - E^0)}{RT}\right) \qquad 7b$$

$$k_{a,0} = exp\left(\frac{-\Delta G_0^*}{RT}\right) exp\left(\frac{\beta F(E_e - E^0)}{RT}\right) \qquad 8a$$

$$k_{a,0} = k_0\, exp\left(\frac{\beta F(E_e - E^0)}{RT}\right) \qquad 8b$$

The shift in electrode potential from the equilibrium potential is called overpotential and is defined as, $\eta = E^0 - E_e$ or $-\eta = E_e - E^0$. For the cathodic reaction, η is positive but negative for anodic reaction. Substituting for $E_e - E^0$ in equations 7b and 8b, generates equations 9 and 10 respectively,

$$k_{c,0} = k_0\, exp\left(\frac{-\alpha F \eta}{RT}\right) \qquad 9$$

$$k_{a,0} = k_0\, exp\left(\frac{\beta F \eta}{RT}\right) \qquad 10$$

The net current in the cell can be gotten from the relation,

$$R_{net} = k_c C_O(0.t) - k_a C_R(0.t) = \frac{i_c - i_a}{nF} = \frac{i}{nF} \qquad 11$$

Therefore,

$$i = F[k_c C_O(0.t) - k_a C_R(0.t)] \qquad 12$$

Substituting equations 9 and 10 into equation 12 leads to equations 13 and 14,

$$i = F\left[C_O k_0 \, exp\left(\frac{-\alpha F \eta}{RT}\right) - C_R k_0 \, exp\left(\frac{\beta F \eta}{RT}\right)\right] \qquad 13$$

$$i = i_0\left[\frac{C_O}{C_0^*} k_0 \, exp\left(\frac{-\alpha F \eta}{RT}\right) - \frac{C_R}{C_R^*} k_0 \, exp\left(\frac{\beta F \eta}{RT}\right)\right] \qquad 14$$

where i_0 is the exchange current density. At equilibrium (dynamic equilibrium), $i_0 = i_c = i_a$. Under this condition, no net current flows across the electrodes but both reduction and oxidation take place at equal rate, so that the composition of the electrolyte does not change. The dynamic flow of electrons or charge in both directions can be written in terms of current densities as follows.

$$i_O = i_A = i_C$$

where I_A is anodic and I_C is cathodic current densities. By convention, anodic current density is given a negative sign and cathodic current density positive sign such that,

$$i_0 = i_{c,e} = F k_0 C_0^* exp\left(\frac{-\alpha F(E_e - E^0\}}{RT}\right) \qquad 15$$

$$i_0 = i_{a,e} = F k_0 C_R^* exp\left(\frac{\beta F(E_e - E^0\}}{RT}\right) \qquad 16$$

where C_0^* and C_R^* are the concentration of the electroactive species in the bulk electrolyte. I_0 is the exchange current density and is defined, as the flow of charge or electrons across an electrochemical system in equilibrium. Normally, its value is very low; often in the order of 10^{-8} A°. It refers to the extent of both oxidation and reduction that occur. The equilibrium situation at an electrode is characterised by equilibrium potential and exchange current density. For a spontaneous reaction, $C_0^* = C_O$ and $C_R^* = C_R$. Therefore, equation 14 translates to equations 17, whish is the Butler-Volmer equation

$$i = i_0\left[exp\left(\frac{-\alpha F \eta}{RT}\right) - exp\left(\frac{\beta F \eta}{RT}\right)\right] \qquad 17$$

(iii) At the extreme condition of over potential being highly negative, cathodic current density increases while anodic current density becomes negligible. At this stage, the first term in the Butler-Volmer equation becomes negligible. The equation can be written as:

$$i = i_0 exp\left(\frac{-\alpha F \eta}{RT}\right) \qquad 1$$

When the over potential is negatively higher than above 52 mV, equation 1 shows that the current changes exponentially with over potential. The current also depends on I_O. Equation 1 may also be written as:

$$logi = logi_0 - \frac{\alpha F\eta}{2.303RT} \quad 2$$

Equation 2 is called cathodic Tafel equation. Similarly, at positive overpotential higher than 52 mV, anodic current density is much higher than cathodic and the cathodic current density become negligible, hence we have:

$$i = i_0 exp\left(\frac{\beta F\eta}{RT}\right) \quad 3$$

$$logi = logi_0 + \frac{\beta F\eta}{2.303RT} \quad 4$$

Equation 2 and 4 are the anodic Tafel equations. When values of logI are plotted against over potential, the straight line obtained is called the Tafel plot. These offer simple method for experimentally determining I_O and the transfer coefficients.

4.0 (i) Self Assessment Exercises

1. (a) Using standard electrode potential cell, calculate the standard free energy change for the following reaction,

$Zn_{(s)} + 2Ag^{+}_{(aq)} = Zn^{2+}_{(aq)} + 2Ag_{(s)}$

(a) Calculate the cell potential for the cell, whose reactions are given below,

$Cd_{(s)} = Cd^{2+}_{(aq)} + 2e^{-} E_{Cd} = -0.40$ V

$Ag^{+}_{(aq)} + e^{-} = Ag_{(s)} E_{Ag} = 0.80$ V

2. Given the following cell, use the Nernst equation to represent the formula for calculating the electrode potential at the cathode, at the anode and the electrode potential of the cell.

$$Mg_{(s)} + 2Ag^{+}(0.001) \rightarrow Mg^{2+}(0.002\,M) + 2Ag_{(s)}$$

Hence if the standard electrode potential of the cell is 2.07, calculate the E_{cell}.

(b) Based on your derivation, predict what will happened to the E_{cell} if the concentration of the Mg^{2+} or Ag^{+} is increase

(c) Calculate the change in free energy of the cell and state whether the cell reaction is spontaneous

(d) Calculate the equilibrium constant of the cell at 298 K

3 (a) Define the term, exchange current density and state its significant in electrochemistry

(b) Given the cathodic and anodic Tafel equations, written as, $i = i_0 exp\left(\frac{-\alpha F\eta}{RT}\right)$ and $i = i_0 exp\left(\frac{\beta F\eta}{RT}\right)$, respectively. Show that the cathodic and anodic Tafel equation can be written as $\eta = a - blogi$ and $\eta = a + blogi$ respectively. Hence state the implication of the derived equations

4. Given that the standard potential of a Daniel cell is -1.10 V, calculate the equilibrium constant for the cell reaction.

5. If the E_{cell} of a cell is 1.10 at 298 K, calculate the equilibrium constant for the cell reaction

Answer to Self Assessment Questions

1(a) The reaction must be broken into a half cell reaction. The half reactions are as follow,

$Zn_{(s)} = Zn^{2+}_{(aq)} + 2e^-$ $E^0 = -0.76$

$2Ag^+_{(aq)} + 2e^- = 2Ag.$ $E^0 = 0.80$

$E_{cell} = 0.80 + 0.76 = 1.56$ V

$\Delta G = -nFE_{cell} = (-2 \times 96500 \times 1.56)$ J = 301.08 kJ/mol

(b) The cell reaction will be spontaneous with the stronger reducing agent, which is the specie with lower value of emf. Thus, Cd will preferentially act as the reducing agent compare to Ag. Therefore, the cell reaction can be written as follows,

$Cd_{(s)} = Cd^{2+} + 2e^-$ E = -0.04 V

$2Ag^+_{(aq)} + 2e^- = 2Ag_{(s)}$ E = 0.80 V

$E_{cell} = E^0_{Ag} - E^0_{Cd} = 0.80 - (-0.40) = 1.20$ V

2. At the cathode, the electrode potential is given as,

$$E_{Ag^+/Ag} = E^0_{Ag^+/Ag} - \frac{RT}{2F} ln\left(\frac{1}{[Ag^+]}\right)$$

$$E_{Ag^+/Ag} = E^0_{Ag^+/Ag} - \frac{RT}{2F} ln\left(\frac{1}{[0.001]}\right)$$

At the anode, the electrode potential is given as,

$$E_{Mg^{2+}/Mg} = E^0_{Mg^{2+}/Mg} - \frac{RT}{2F} ln\left(\frac{1}{[Mg^{2+}]}\right)$$

$$E_{Mg^{2+}/Mg} = E^0_{Mg^{2+}/Mg} - \frac{RT}{2F} ln\left(\frac{1}{[0.002]}\right)$$

The cell potential will be given as,

$$E_{cell} = E_{Ag^+/Ag} - E_{Mg^{2+}/Mg}$$

$$E_{cell} = \left(E^0_{Ag^+/Ag} - E^0_{Mg^{2+}/Mg}\right) - \frac{RT}{2F} ln\left(\frac{1}{[Ag^+]}\right) - \frac{RT}{2F} ln\left(\frac{1}{[Mg^{2+}]}\right)$$

$$E_{cell} = \left(E^0_{Ag^+/Ag} - E^0_{Mg^{2+}/Mg}\right) - \frac{RT}{2F}\left\{ln\left(\frac{1}{[Ag^+]}\right) - ln\left(\frac{1}{[Mg^{2+}]}\right)\right\}$$

$$E_{cell} = E^0_{cell} - \frac{RT}{2F} ln\left(\frac{[Mg^{2+}]}{[Ag^+]}\right)$$

$$E_{cell} = 3.07 - \frac{0.059}{2} log\left(\frac{[0.002]}{[0.001]}\right) = 3.06\ V$$

(b) Based on the equation, $E_{cell} = E^0_{cell} - \frac{RT}{2F} ln\left(\frac{[Mg^{2+}]}{[Ag^+]}\right)$, Increase in the concentration of Ag^+ will increase the emf of the cell while increase in the concentration of Mg^{2+} will decrease the emf of the cell.

(c) The change in free energy is related to the cell potential according to the equation, $\Delta G = -nFE_{cell}$. Therefore, $\Delta G = -2\ x\ 96489\ x\ 3.06 = -590.512\ kJ/mol$. The cell reaction is spontaneous because the change in free energy is negative.

(d) The equilibrium constant of the reaction is related to the equilibrium constant according to the equation, $\Delta G = -RTlnK_C$. Therefore,

$lnK_C = \frac{-\Delta G}{RT} = \frac{590512 J/mol}{(8.314 J/mol/K)(298\ K)} = 238.34$, which gives $K_C = 3.24 \times 10^{103}$.

3. (a) Exchange current density, i_0 is the equilibrium current obtained when the anodic and cathodic current are equal. i.e., at equilibrium (dynamic equilibrium), $i_0 = i_c = ia$. Under this condition, no net current flows across the electrodes but both reduction and oxidation take place at equal rate, so that the composition of the electrolyte does not change. The dynamic flow of electrons or charge in both directions can be written in terms of current densities as follows.

$$i_O = i_A = i_C$$

where I_A is anodic and I_C is cathodic current densities. By convention, anodic current density is given a negative sign and cathodic current density positive sign.

(b) Given, $i = i_0 exp\left(\frac{-\alpha F\eta}{RT}\right)$, we can re-arrange the equation to the form,

$$ln\left(\frac{i}{i_0}\right) = \frac{-\alpha F\eta}{RT} \quad \text{(i)}$$

$$\eta = \frac{2.303RT}{\alpha F} logi_0 - \frac{2.303RT}{\alpha F} logi \quad \text{(ii)}$$

$$\eta = a - blogi \quad \text{(iii)}$$

where a = $\frac{2.303RT}{\alpha F} logi_0$ and b = $\frac{2.303RT}{\alpha F}$. Equation (iii) also shows that for the cathodic reaction, a plot of overpotential versus logic is linear with slope and intercept equal to $\frac{2.303RT}{\alpha F}$ and $\frac{2.303RT}{\alpha F} logi_0$ respectively. Similarly, for the anodic reaction, $i = i_0 exp\left(\frac{\beta F\eta}{RT}\right)$.

Rearranging the equations, we have

$$ln\left(\frac{i}{i_0}\right) = \frac{\beta F\eta}{RT} \quad \text{(iv)}$$

$$2.303logi - 2.303logi_0 = \frac{\beta F\eta}{RT} \quad \text{(v)}$$

$$\eta = -\frac{2.303RT}{\beta F} logi_0 + \frac{2.303RT}{\beta F} logi \quad \text{(vi)}$$

$$\eta = a + blogi \quad \text{(vii)}$$

Again, equation 7 reveals that for the anodic reaction, a plot of overpotential against log(i) is linear with slope and intercept equal to a and b respectively. where a = $\frac{-2.303RT}{\beta F}$ and b = $\frac{2.303RT}{\beta F}$.

The Butler-Volmer equation can be reduced to the Tafel equations for the cathodic and anodic reactions.

5. The change in free energy is related to the electrode potential and equilibrium constant according to the following equations,

$$\Delta G = -nFE^0$$

$$\Delta G = -RTlnk$$

Therefore,

$$-RTlnk = -nFE^0$$

$$lnk = \frac{nFE^0}{RT} = \frac{2 \times (96485 \times 10^4\ C) \times (1.10\ V)}{(8.3145\ J/mol/K)(298.15\ K)} = 42.15$$

$$K = 1.5 \times 10^{17}$$

(ii) Class Activity

(1) Based on the value of cell equilibrium constant explain if the cell reactions (at 303 K and n = 2) in cells with the following electrode potentials are spontaneous or not (i) 2.27 V (ii) -2.27 V (iii) 3.47 (iv) -3.47 (10 minutes)

(2) A given cell at 300 K has E_{cell} value of 0.98 V. Calculate the standard free energy of the cell and state if the cell reaction is spontaneous or not (n = 3) (4 minutes)

5.0 Conclusion

Polarization is a concept that has led to the progress of numerous industrial phenomena. Corrosion is perhaps one of the most widely studied fields using the concept of polarization. Corrosion is an electrochemical process involving the corrosion of the anode (where oxidation

takes place). Instrumentation in corrosion using polarization theory involves the production of linear polarization curve and potentiodynamic polarization curve. Several successes have been recorded on the use of polarization technique to study the inhibition of the corrosion of metals such as mild steel, aluminium, etc. Further details on the use of polarization techniques on corrosion are provided in the journal references provided at the end of this unit.

6.0 Summary

The essential theory in polarization of electrochemical interphases is the one that has been presented by Tafel. It should be noted that several parameters can be deduced from Tafel plots. For example, the slopes of the anodic and cathodic plots give the values of β_a and β_b respectively. If we extrapolate the point of interception of the two plots to the y-axis and x-axis, we have the potential and the current density respectively.

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Link to slide show:https://www.slideshare.net/GamryInstruments/echem-basics-for-users

MODULE 2

STUDY UNIT 2: VERIFICATION OF TAFEL EQUATION: BUTLER VOLMER LAW

3.0 Introduction

4.0 Intended Learning Outcome

3.0 Main Content

3.1 Derivation of Butler Volmer equation

3.3 Experimental determination of current and Tafel plot

3.3.1 Significance of Tafel plot

3.3 Concentration potential

3.4 Total overpotential

4.0 (i) Self Assessment Exercise and Answers

(ii) Class Activity

5.0 Conclusion

6.0 Summary

7.0 References/Further Reading

1.0 Introduction

Prof. Julius Tafel was a Lecturing organic Chemistry in Chemical Institute, Wurzburg University, Germany up to 1893. However, after 1893 he lectured physical and general chemistry. By German tradition, this would include lots of electrochemistry, and lots of experimentation. With strychnine reduction, Tafel had truly turned electrochemist. A careful observer, Tafel soon was able to summarize his major and rather far-reaching general deductions from his experimental work. He is regarded as one of the fathers of electrochemistry In this unit, we shall examine some of the basic findings of Tafel laws and the modification and application of his findings.

2.0 Learning Outcomes

When you have studied this session, you should be able to:

i. understand the irreversible behaviour of an electrode.
ii. Understand the mechanism of electron transfer to an electrode.
iii. Understand the mechanism of electron transfer to an electrode
iv. Determine the current density.
v. Derive the Butler Volmer equation
vi. Verify Tafel equation

vii. interpret Evan's diagram

3.0 Main Content

3.1 Derivation of Butler Volmer equation

Tafel equation governs the irreversible behaviour of an electrode. Consider an electrolyte in which an inert or noble electrode is kept immersed. It is called working electrode, (WE). Also assume that an oxidised and a reduced species are present near the electrode and exhibit the following electron transfer reaction.

$$Oxid + e^- = Red \qquad 4.1$$

Oxidis the oxidised specie and Redis the reduced specie present at equilibrium and is stable in the solution. Let us assume that no other electron transfer reaction other than the above, occurs in the cell. if the concentration of Oxid and Red are C_o and C_R respectively and they are very low. An inert electrolyte is also present to minimise IR drop. Along with WE, a reference electrode RE is also kept immersed, to form the cell. Since the potential of RE is constant, variation in cell emf is the variation in the potential of the WE and vice versa. The rate of cathodic (R_C) and anodic (R_a) reactions can be written as follows,

$$R_c = k_c C_O\,(0.t) \qquad 4.2$$

$$R_a = k_a C_R\,(0.t) \qquad 4.3$$

The net rate is the difference, i.e., $R_{net} = R_c - R_a$, therefore,

$$R_{net} = k_c C_O(0.t) - k_a C_R\,(0.t) \qquad 4.4$$

The cathodic and anodic rate constants vary with temperature according to the following equation,

$$k_c = exp\left(\frac{-\Delta G_c^*}{RT}\right) \qquad 4.5$$

$$k_a = exp\left(\frac{-\Delta G_a^*}{RT}\right) \qquad 4.6$$

At equilibrium, $R_a = R_c$ and $k_c C_O(0.t) = k_a C_R\,(0.t)$. The equilibrium constant can be defined as the ratio of R_a to that of R_c. Therefore,

$$\frac{k_a}{k_c} = \frac{C_O\,(0,t)}{C_R\,(0,t)} = \frac{exp\left(\frac{-\Delta G_a^*}{RT}\right)}{exp\left(\frac{-\Delta G_c^*}{RT}\right)} = exp\left(\frac{-\Delta G_a^*}{RT} + \frac{\Delta G_c^*}{RT}\right) = exp\left(\frac{\Delta G_c^*}{RT} - \frac{\Delta G_a^*}{RT}\right) \qquad 4.7$$

Simplification of equation 4.7 yields equation 4.8

$$ln\left(\frac{C_O\,(0,t)}{C_R\,(0,t)}\right) = ln\left(\frac{k_{a,0}}{k_{c,0}}\right) = \frac{\Delta G_c^* - \Delta G_a^*}{RT} \qquad 4.8$$

Application of the Nernst equation to the above equilibrium process leads to equation 4.9,

$$E_e = E^0 + \frac{RT}{F} ln\left(\frac{C_0}{C_R}\right) \qquad 4.9a$$

$$ln\left(\frac{C_0}{C_R}\right) = \frac{F}{RT}(E_e - E^0) \quad 4.9b$$

Since $ln\left(\frac{C_0}{C_R}\right) = \frac{\Delta G_c^* - \Delta G_a^*}{RT}$, equation 4.10b becomes,

$$\frac{\Delta G_c^* - \Delta G_a^*}{RT} = \frac{F}{RT}(E_e - E^0) \quad 4.10a$$

$$\Delta G_c^* - \Delta G_a^* = F(E_e - E^0) \quad 4.10b$$

Equation 35b can be separated for the cathodic and for the anodic reactions by introducing a symmetry factor called the transfer coefficient, α and β respectively. α is the transfer coefficient for the cathode and β is the transfer coefficient for the anode. β = 1- α. Therefore, α + β = 1 and the following equations are hereby obtained,

$$\Delta G_c^* = \Delta G_0^* + \alpha F(E_e - E^0) \quad 4.11$$

$$\Delta G_a^* = \Delta G_0^* - \beta F(E_e - E^0) \quad 4.12$$

Application of equation 4.4 and 4.5, further simplifies equations 4.11 and 4.12 into 4.13 and 4.13 respectively,

$$k_{c,0} = exp\left(\frac{-\Delta G_0^*}{RT}\right) exp\left(\frac{-\alpha F(E_e - E^0)}{RT}\right) \quad 4.13a$$

$$k_{c,0} = k_0\, exp\left(\frac{-\alpha F(E_e - E^0)}{RT}\right) \quad 4.13b$$

$$k_{a,0} = exp\left(\frac{-\Delta G_0^*}{RT}\right) exp\left(\frac{\beta F(E_e - E^0)}{RT}\right) \quad 4.14a$$

$$k_{a,0} = k_0\, exp\left(\frac{\beta F(E_e - E^0)}{RT}\right) \quad 4.14b$$

The shift in electrode potential from the equilibrium potential is called overpotential and is defined as, $\eta = E^0 - E_e$ or $-\eta = E_e - E^0$. For the cathodic reaction, η is positive but negative for anodic reaction. Substituting for $E_e - E^0$ in equations 4.13b and 4.14b, generates equations 4.15 and 4.16 respectively,

$$k_{c,0} = k_0\, exp\left(\frac{-\alpha F\eta}{RT}\right) \quad 4.15$$

$$k_{a,0} = k_0\, exp\left(\frac{\beta F\eta}{RT}\right) \quad 4.16$$

The net current in the cell can be gotten from the relation,

$$R_{net} = k_c C_O(0.t) - k_a C_R(0.t) = \frac{i_c - i_a}{nF} = \frac{i}{nF} \quad 4.17$$

Therefore,

$$i = F[\,k_c C_O(0.t) - k_a C_R(0.t)] \quad 4.18$$

Substituting equations 40 and 41 into equation 4.18 leads to equations 4.19 and 4.20,

$$i = F\left[C_O k_0\, exp\left(\frac{-\alpha F\eta}{RT}\right) - C_R k_0\, exp\left(\frac{\beta F\eta}{RT}\right)\right] \quad 4.19$$

$$i = i_0 \left[\frac{C_O}{C_0^*} k_0 \, exp\left(\frac{-\alpha F \eta}{RT}\right) - \frac{C_R}{C_R^*} k_0 \, exp\left(\frac{\beta F \eta}{RT}\right) \right] \qquad 4.20$$

where i_0 is the exchange current density. At equilibrium (dynamic equilibrium), $i_0 = i_c = i_a$. Under this condition, no net current flows across the electrodes but both reduction and oxidation take place at equal rate, so that the composition of the electrolyte does not change. The dynamic flow of electrons or charge in both directions can be written in terms of current densities as follows.

$$i_O = i_A = i_C$$

where I_A is anodic and I_C is cathodic current densities. By convention, anodic current density is given a negative sign and cathodic current density positive sign such that,

$$i_0 = i_{c,e} = F k_0 C_0^* exp\left(\frac{-\alpha F(E_e - E^0\}}{RT}\right) \qquad 4.21$$

$$i_0 = i_{a,e} = F k_0 C_R^* exp\left(\frac{\beta F(E_e - E^0\}}{RT}\right) \qquad 4.22$$

where C_0^* and C_R^* are the concentration of the electroactive species in the bulk electrolyte. I_O is the exchange current density and is defined, as the flow of charge or electrons across an electrochemical system in equilibrium. Normally, its value is very low; often in the order of 10^{-8} A°. It refers to the extent of both oxidation and reduction that occur. The equilibrium situation at an electrode is characterised by equilibrium potential and exchange current density. For a spontaneous reaction, $C_0^* = C_O$ and $C_R^* = C_R$. Therefore, equation 4.22 translates to equations 4.23

$$i = i_0 \left[exp\left(\frac{-\alpha F \eta}{RT}\right) - exp\left(\frac{\beta F \eta}{RT}\right) \right] \qquad 4.23$$

Equation 48 is the Butler Volmer equation. The Butler–Volmer equation (also known as Erdey-Grúz-Volmer equation) is one of the most fundamental relationships in electrochemical kinetics. It describes how the electrical current on an electrode depends on the electrode potential, under the assumption that both the cathodic and anodic reactions occur at the same electrode. The equation shows that the measure current density is a function of

i. overpotential (η),
ii. exchange current density (I_O)
iii. anodic and cathodic transfer coefficients.

In addition, the equation further reveals that the current density at any over potential is the sum of cathodic and anodic current densities. At the extreme condition of over potential being highly negative, cathodic current density increases while anodic current density becomes negligible. At this stage, the first term in the Butler-Volmer equation becomes negligible. The equation can be written as:

$$i = i_0 exp\left(\frac{-\alpha F\eta}{RT}\right) \quad 4.24$$

When the over potential is negatively higher than above 52 mV, equation 4.24 shows that the current changes exponentially with over potential. The current also depends on I_O. Equation 4.24 may also be written as:

$$logi = logi_0 - \frac{\alpha F\eta}{2.303RT} \quad 4.25$$

Equation 4.25 is called cathodic Tafel equation. Similarly, at positive overpotential higher than 52 mV, anodic current density is much higher than cathodic and the cathodic current density become negligible, hence we have:

$$i = i_0 exp\left(\frac{\beta F\eta}{RT}\right) \quad 4.26$$

$$logi = logi_0 + \frac{\beta F\eta}{2.303RT} \quad 4.27$$

Equation 4.26 and 4.27 are the anodic Tafel equations. When values of logI are plotted against over potential, the straight line obtained is called the Tafel plot. These offer simple method for experimentally determining I_O and the transfer coefficients. We can also simplify the cathodic and anodic Tafel equations as follows,

$$i = i_0 exp\left(\frac{-\alpha F\eta}{RT}\right)$$

$$ln\left(\frac{i}{i_0}\right) = \frac{-\alpha F\eta}{RT}$$

$$\eta = \frac{2.303RT}{\alpha F} logi_0 - \frac{2.303RT}{\alpha F} logi$$

$$\eta = a - blogi \quad 4.28$$

where a = $\frac{2.303RT}{\alpha F} logi_0$ and b = $\frac{2.303RT}{\alpha F}$. Equation 45 also shows that for the cathodic reaction, a plot of overpotential versus logi is linear with slope and interceptequal to $\frac{2.303RT}{\alpha F}$ and $\frac{2.303RT}{\alpha F} logi_0$ respectively. Similarly, for the anodic reaction,

$$i = i_0 exp\left(\frac{\beta F\eta}{RT}\right)$$

$$ln\left(\frac{i}{i_0}\right) = \frac{\beta F\eta}{RT}$$

$$2.303logi - 2.303logi_0 = \frac{\beta F\eta}{RT}$$

$$\eta = -\frac{2.303RT}{\beta F} logi_0 + \frac{2.303RT}{\beta F} logi$$

$$\eta = a + blogi \quad 4.29$$

Again, equation 4. reveals that for the anodic reaction, a plot of overpotential against $logi$ is linear with slope and intercept equal to a and b respectively. where a = $\frac{-2.303RT}{\beta F}$ and b = $\frac{2.303RT}{\beta F}$. Thus, that the Butler-Volmer equation reduces to the Tafel equations for the cathodic and anodic reactions.

3.2 Experimental Determination of *I* and Tafel Plot

The test electrode is kept immersed in its salt solution. The solution should be very dilute so that the concentration near the surface of the electrode does not differ too much from the bulk concentration. A calomel electrode is kept very close to the test electrode. An inert electrode is also taken which serves as the counter electrode. A DC potential is applied across the test and the counter electrodes, making the test electrode negative. This establishes a potential across the test and the reference electrodes which is read by a very sensitive voltmeter connected in the circuit. From this value the rest potential is subtracted to get the applied potential component on the test electrode. An ammeter connected in series reads the current passing through the circuit. The applied potential is increased which increases the over potential on the cathode (test electrode is made more negative) and the corresponding current value is measured (ammeter reading). In this way the current values are taken for several over potential values making test electrode more and more negative. The log values of these current values are plotted against the over potential on one side.
In the next step the test electrode is connected to the positive terminal and the counter to negative. As done earlier the current is measured for various over potential values and plotted against them on the other side of the graph.

3.2.1 Significance of Tafel Plots

The point of intersection on the Y axis of the extrapolated graph gives the value of I_0, the exchange current density, which is otherwise very difficult to determine. It the current passing at equilibrium conditions and a very low value.

1. The transfer coefficients can be determined; from the anodic slope,α_A and from cathodic slopeα_C can be determined. This value is very important in industrial practice. This determines the potential that is to be applied to affect the desired rate of reduction or oxidation.
2. Knowing the value of transfer coefficient for a reaction the number of electrons, n, for an unknown reaction can be determined. This reflects on the mechanism of the reaction; that is how many electrons are involved in that step. Whether the reaction is single step or multi step is revealed by this value.

3. The effect of α_C on current density is shown in Fig. 4.1.

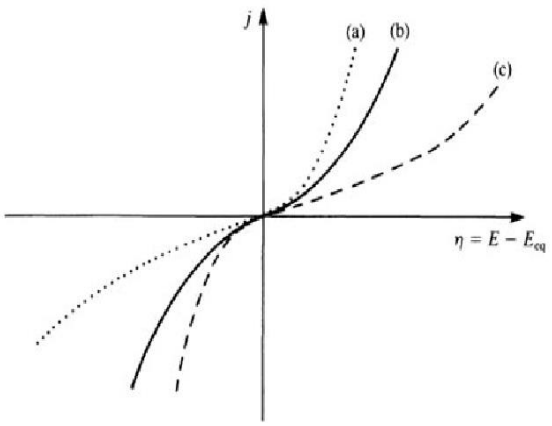

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Fig. 4.1: The effect of a on the current density, j. (a) α_C = 0.25: oxidation favoured; (b) α_C = 0.50: symmetric (c) α_C = 0.75: reduction favoured

As cathodic transfer coefficient value increases reduction is favoured and oxidation is not favoured and vice versa for anodic transfer coefficient. The transfer coefficients depend on the pH of the medium; in acidic conditions (low pH) reduction is favoured which is revealed by an increase in α_C

3.3 Concentration over potential

When the current applied to an electrochemical cell is high, cations involved in cathodic reactions are depleted due to metal ion reduction (i.e., $M^{n+} + ne^- \rightarrow M$). Consequently, diffusion and convection are the major mass transport processes that are responsible for transporting cations from the bulk solution to the electrode surface. The ion concentration near the surface of the electrode depends on diffusion while the process of convection controls the transportation of ions from the bulk solution.

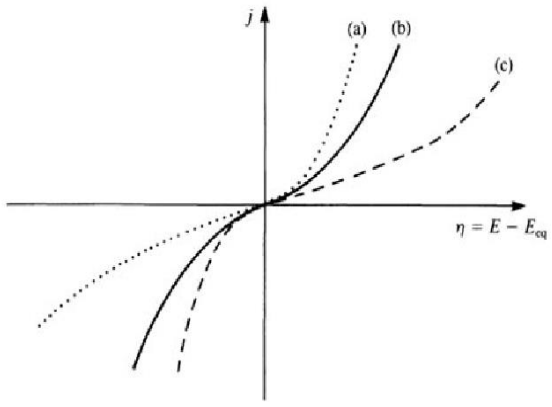


Fig. 4.2: The effect of a overpotential on the current density, j. (a) α= 0.25: oxidation favoured; (b) α= 0.50: symmetric (c) α= 0.75: reduction favoured

If the concentration of the cations varies from C_s, near the surface to the electrode to C_B, (i.e. in the bulk concentration) across the cathode over a distance (δ), we define the concentration gradient as follows,

$$Concentrationgradient = \frac{dC}{dx} = \frac{(C_B - C_S)}{\delta} \qquad 4.30$$

According to Fick's first law, current density (J) is proportional to the concentration gradient. Therefore, J is defined as the product of concentration gradient and diffusion coefficient (D_{ion}) as shown below,

$$J = D_{ion}\frac{(C_B - C_S)}{\delta} \qquad 4.31$$

where D_{ion} is the diffusion coefficient. Also, cathodic current is defined as nFJ and can be expressed according to equation 4.32,

$$i_C = nFJ = nFD_{ion}\frac{(C_B - C_S)}{\delta} \qquad 4.32$$

However, maximum current is obtained when the concentration of ions at the surface is equal to zero (i.e. $C_S = 0$) and the current obtained at the cathode under this condition is called limiting cathodic current (i.e., $i_{max,\,C} = i_L$). Hence equation 4.32 becomes,

$$i_L = nFD_{ion}\frac{C_B}{\delta} \qquad 4.33$$

Two extreme conditions can be linked to C_B and C_S and they can be resolved using the Nernst equation. The first condition is before current flow while the second condition is after current flow. Application of the Nernst equation to these two conditions yield equations 4.34 and 4.35 respectively

$$E_i = E^0 + \frac{2.3RT}{nF} log\left(\frac{[C_B]}{1}\right) \qquad 4.34$$

$$E_f = E^0 + \frac{2.3RT}{nF} log\left(\frac{[C_S]}{1}\right) \qquad 4.35$$

Concentration cathodic overpotential would be defined as E_f - E_i and is equal to

$$E_f - E_i = \frac{2.3RT}{nF} log\left(\frac{[C_S]}{1}\right) - \frac{2.3RT}{nF} log\left(\frac{[C_B]}{1}\right) = \frac{2.3RT}{nF} log\left(\frac{[C_S]}{[C_B]}\right) \qquad 4.36$$

From equation 4.32, $i_C = nFJ = nFD_{ion}\frac{(C_B - C_S)}{\delta}$, therefore

$$C_B - C_S = \frac{nFJ\delta}{nFD_{ion}} = \frac{i_c\delta}{nFD_{ion}} \text{ (note, the cathodic current, } i_c = nFJ)$$

$$-C_S = \frac{nFJ\delta}{nFD_{ion}} - C_B = \frac{i_c\delta}{nFD_{ion}} - C_B*$$

$$C_S = C_B - \frac{i_c\delta}{nFD_{ion}} \qquad 4.37$$

From equation 58, $i_L = nFD_{ion}\frac{C_B}{\delta}$ which implies that

$$C_B = \frac{i_L\delta}{nFD_{ion}} \quad 4.38$$

Therefore,

$$C_S = C_B - \frac{i_c\delta}{nFD_{ion}} = \frac{i_L\delta}{nFD_{ion}} - \frac{i_c\delta}{nFD_{ion}} \quad 4.39$$

Substituting for the cathodic overpotential becomes

$$E_f - E_i = \eta_{C,Con} = \frac{2.3RT}{nF} log\left(\frac{\frac{i_L\delta}{nFD_{ion}} - \frac{i_c\delta}{nFD_{ion}}}{\frac{i_L\delta}{nFD_{ion}}}\right) \quad 4.40$$

$$\boldsymbol{\eta_{C,Con} = \frac{2.3RT}{nF} log\left(\frac{i_L - i_c}{i_L}\right)} \quad 4.41$$

$$\boldsymbol{\eta_{C,Con} = \frac{2.3RT}{nF} log\left[1 - \frac{i_C}{i_L}\right]} \quad 4.42$$

From equation 4.42, we can examine the effect of i_L on $\eta_{C,Con}$ as follows,

i. If $i_c << i_L$, then the ratio, $\frac{i_C}{i_L}$ will tend to zero and $\eta_{C,Con} = \frac{2.3RT}{nFD_{ion}} log[1]$, which is equal to 0

ii. If $i_c \approx i_L$, then the ratio, $\frac{i_C}{i_L}$ will be equal to unity and $\eta_{C,Con} = \frac{2.3RT}{nFD_{ion}} log[0]$, will be equal to infinity.

3.4 Total polarization for a single electrode

In summary, total polarization can be separated into total anodic and total cathodic polarization as follows,

Total anodic polarization: $\eta_{T,a} = \eta_{act,a} = \beta_a log\left(\frac{i_a}{i_0}\right)$

Total cathodic polarization: $\eta_{T,C} = \eta_{act,C} + \eta_{con,C} = \beta_C log\left(\frac{i_C}{i_0}\right) + \frac{2.3RT}{nFD_{ion}} log\left[1 - \frac{i_C}{i_L}\right]$

The above concept can be summarised graphically as shown in Fig. 4.3, which represents, Evans diagram. In summary, activation polarization can occur in the anode and the cathode while concentration polarization is common at the cathode.

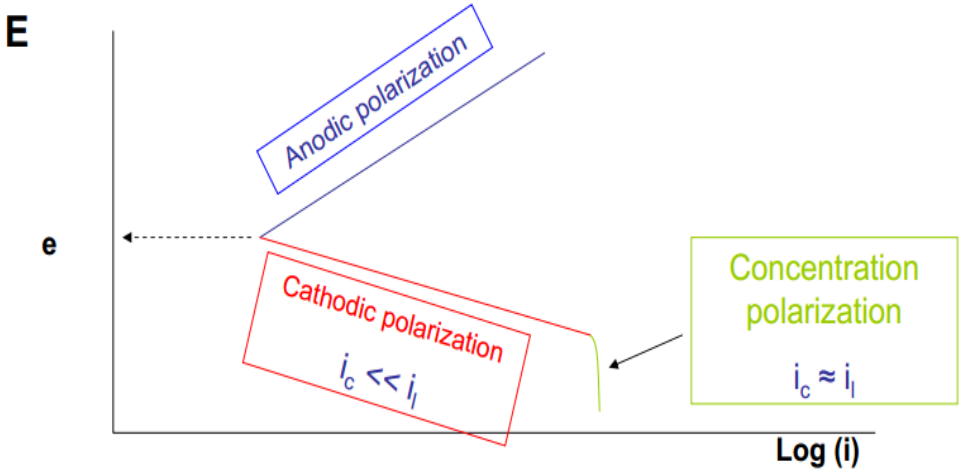


Fig. 4.3: Evans diagram showing anodic and cathodic polarizations

Worked example 1

In a Cu^{2+}/Cu electrochemical cell, given that the concentration of the cations varies from C_s, near the surface to C_B, (i.e. in the bulk concentration) across the cathode over a distance (δ). Answer the following questions,

(a) Derive an expression for the concentration gradient

(b) State Fick's first law and relate the law to the concentration gradient

(c) Derive expressions for cathodic current, limiting cathodic current and hence derive an equation for concentration over potential of the cell. Hence calculate the overpotential at 303 K, when the cathodic and limiting cathodic current are equal to 0.6 A and 1.2 A respectively.

(d) From the derive expression, state the expectation for the two extreme conditions that the derive equation (cathodic over potential) can yield.

Solution

(a) The concentration gradient can be defined as,

$$Concentrationgradient = \frac{dC}{dx} = \frac{(C_B - C_S)}{\delta} \qquad 1$$

(b) According to Fick's first law, current density (J) is proportional to the concentration gradient. Therefore, J is defined as the product of concentration gradient and diffusion coefficient (D_{ion}) as shown below,

$$J = D_{ion}\frac{(C_B - C_S)}{\delta} \qquad 2$$

where D_{ion} is the diffusion coefficient.

(c) Cathodic current is defined as nFJ and can be expressed according to equation 3,

$$i_C = nFJ = nFD_{ion}\frac{(C_B - C_S)}{\delta} \quad 3$$

However, maximum current is obtained when the concentration of ions at the surface is equal to zero (i.e. $C_S = 0$) and the current obtained at the cathode under this condition is called limiting cathodic current (i.e., $i_{max,\,C} = i_L$). Hence equation 3 becomes,

$$i_L = nFD_{ion}\frac{C_B}{\delta} \quad 4$$

Two extreme conditions can be linked to C_B and C_S and they can be resolved using the Nernst equation. The first condition is before current flow while the second condition is after current flow. Application of the Nernst equation to these two conditions yield equations 5 and 6 respectively

$$E_i = E^0 + \frac{2.3RT}{nF} log\left(\frac{[C_B]}{1}\right) \quad 5$$

$$E_f = E^0 + \frac{2.3RT}{nF} log\left(\frac{[C_S]}{1}\right) \quad 6$$

Concentration cathodic overpotential would be defined as E_f - E_i and is equal to

$$E_f - E_i = \frac{2.3RT}{nF} log\left(\frac{[C_S]}{1}\right) - \frac{2.3RT}{nF} log\left(\frac{[C_B]}{1}\right) = \frac{2.3RT}{nF} log\left(\frac{[C_S]}{[C_B]}\right) \quad 7$$

From equation 49, $i_C = nFJ = nFD_{ion}\frac{(C_B - C_S)}{\delta}$, therefore

$$C_B - C_S = \frac{nFJ\delta}{nFD_{ion}} = \frac{i_c\delta}{nFD_{ion}} \text{ (note, the cathodic current, } i_c = nFJ)$$

$$-C_S = \frac{nFJ\delta}{nFD_{ion}} - C_B = \frac{i_c\delta}{nFD_{ion}} - C_B*$$

$$C_S = C_B - \frac{i_c\delta}{nFD_{ion}} \quad 8$$

From equation 4, $i_L = nFD_{ion}\frac{C_B}{\delta}$ which implies that

$$C_B = \frac{i_L\delta}{nFD_{ion}} \quad 9$$

Therefore,

$$C_S = C_B - \frac{i_c\delta}{nFD_{ion}} = \frac{i_L\delta}{nFD_{ion}} - \frac{i_c\delta}{nFD_{ion}} \quad 10$$

Substituting for C_B (equation 9) and C_S (equation 10), the cathodic overpotential becomes

$$E_f - E_i = \eta_{C,Con} = \frac{2.3RT}{nF} log\left(\frac{\frac{i_L\delta}{nFD_{ion}} - \frac{i_c\delta}{nFD_{ion}}}{\frac{i_L\delta}{nFD_{ion}}}\right) \quad 11$$

$$\boldsymbol{\eta_{C,Con} = \frac{2.3RT}{nF} log\left(\frac{i_L - i_c}{i_L}\right)} \quad 12$$

$$\boldsymbol{\eta_{C,Con} = \frac{2.3RT}{nF} log\left[1 - \frac{i_C}{i_L}\right]} \quad 13$$

when i_C = 0.6 A and i_L = 1.2 A, then,

$$\eta_{C,Con} = \frac{2.3x303x\ 8.314}{2x96500} log\left[1 - \frac{0.6}{1.2}\right] = -0.00904\ V$$

(d) From equation 13, we can examine the effect of i_L on $\eta_{C,Con}$ as follows,

i. If $i_c << i_L$, then the ratio, $\frac{i_C}{i_L}$ will tend to zero and $\eta_{C,Con} = \frac{2.3RT}{nFD_{ion}} log[1]$, which is equal to 0

ii. If $i_c \approx i_L$, then the ratio, $\frac{i_C}{i_L}$ will be equal to unity and $\eta_{C,Con} = \frac{2.3RT}{nFD_{ion}} log[0]$, will be equal to infinity.

4.0 (i) Self Assessment Exercise and Answers

1. Using Tafel equation, calculate the exchange current density at overpotential of +0.5 V and the current density of +0.2 A/cm^2 if the transfer coefficient is 0.5 and temperature is 25°C.
2. Calculate the exchange current density if the overpotential (in question 1) is -0.5 V

3. Consider the following equation and answers the questions that follow.

$$i = i_0 \left[exp\left(\frac{-\alpha F\eta}{RT}\right) - exp\left(\frac{\beta F\eta}{RT}\right)\right]$$

(i) What is the name given to the equation?

(ii) What is the significant of the equation in electrochemistry

(iii) With the aids of suitable chemical equations, describe what can be deduced from the equation at extreme condition, i.e. when the cathodic or anodic current is very high

4. With the aid of equations, use Evans diagram to explain total polarization at a single electrode,
5. A Tafel plot (a plot of $logi$ versus η at 273 K) gave slope values of 0.5 and intercept of 0.002. Calculate the exchange current density, and the anodic transfer coefficient.

Answers to Self Assessment Exercises

1. Given

Current density i = +0.2 A/cm^3 = 0.2 x 10^{-6} A/m^3
Overvoltage, η = 0.5 V
Transfer coefficient, β = 0.5
Gas constant = 8.314 J/K
Faraday's constant = 96500 C
Temperature = 273+25 =298K
Exchange current density, i_0 = ?
When the overpotential is positively higher than 52 mV (0.052V), the Tafel equation that is applicable is

$$i = i_0 exp\left(\frac{\beta F \eta}{RT}\right)$$

From the Logarithm of both sides of the equation,

$$\log(i) = \log(i_0) + \frac{\beta F \eta}{RT}$$

$$\log(i_0) = \log(i) - \frac{\beta F \eta}{RT}$$

$$\log(i_0) = \log(0.2 \times 10^{-6}\, Am^3) - \frac{0.5 \times 96500C \times 0.5\, V}{8.314\, JK^{-1} \times 298\, K} = 3.6367 \times 10^{-17}\, Am^3$$

2. **Given**

Current density i = +0.2 A/cm^3 = 0.2 x 10^{-6} A/m^3

Overvoltage, η = -0.5 V

Transfer coefficient, α = 0.5

Gas constant = 8.314 J/K

Faraday's constant = 96500 C

Temperature = 273+25 =298K

Exchange current density, i_o = ?

When the overpotential is negatively higher than -52 mV (-0.052V), the Tafel equation that is applicable is

$$i = i_0 exp\left(\frac{-\alpha F \eta}{RT}\right)$$

From the Logarithm of both sides of the equation,

$$\log(i) = \log(i_0) - \frac{\alpha F \eta}{RT}$$

$$\log(i_0) = \log(i) + \frac{\alpha F \eta}{RT}$$

$$\log(i_0) = \log(0.2 \times 10^{-6}\, Am^3) + \frac{0.5 \times 96500C \times 0.5\, V}{8.314\, JK^{-1} \times 298\, K} = 1093.788\, Am^3$$

3 (i) The Butler–Volmer equation (also known as Erdey-Grúz-Volmer equation) is one of the most fundamental relationships in electrochemical kinetics. It describes how the electrical current on an electrode depends on the electrode potential, under the assumption that both the cathodic and anodic reactions occur at the same electrode.

(ii) The equation shows that the measure current density is a function of

i. overpotential (η),

ii. exchange current density (I_O)

iii. anodic and cathodic transfer coefficients.

In addition, the equation further reveals that the current density at any over potential is the sum of cathodic and anodic current densities.

(iii) At the extreme condition of over potential being highly negative, cathodic current density increases while anodic current density becomes negligible. At this stage, the first term in the Butler-Volmer equation becomes negligible. The equation can be written as:

$$i = i_0 exp\left(\frac{-\alpha F\eta}{RT}\right) \qquad 1$$

When the over potential is negatively higher than above 52 mV, equation 1 shows that the current changes exponentially with over potential. The current also depends on I_O. Equation 1 may also be written as:

$$logi = logi_0 - \frac{\alpha F\eta}{2.303RT} \qquad 2$$

Equation 2 is called cathodic Tafel equation. Similarly, at positive overpotential higher than 52 mV, anodic current density is much higher than cathodic and the cathodic current density become negligible, hence we have:

$$i = i_0 exp\left(\frac{\beta F\eta}{RT}\right) \qquad 3$$

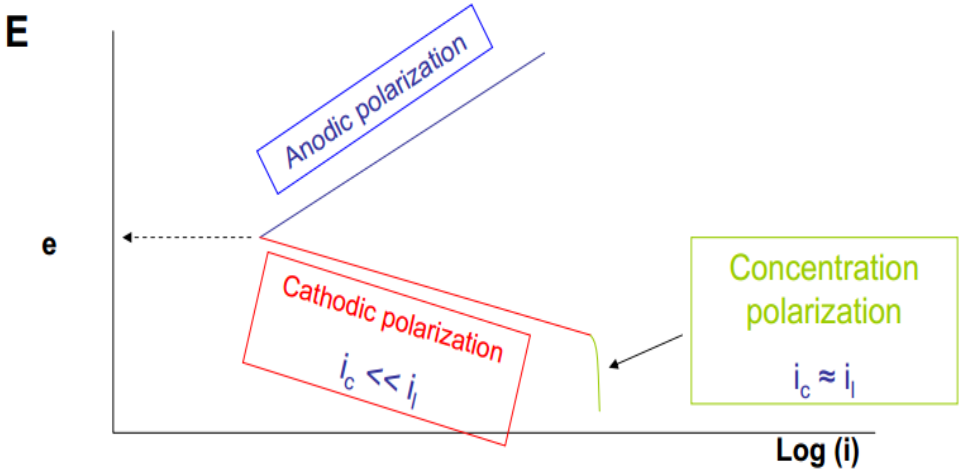
$$logi = logi_0 + \frac{\beta F\eta}{2.303RT} \qquad 4$$

4. Total polarization can be separated into total anodic and total cathodic polarization as follows,

Total anodic polarization: $\eta_{T,a} = \eta_{act,a} = \beta_a log\left(\frac{i_a}{i_0}\right)$

Total cathodic polarization: $\eta_{T,C} = \eta_{act,C} + \eta_{con,C} = \beta_C log\left(\frac{i_C}{i_0}\right) + \frac{2.3RT}{nFD_{ion}} log\left[1 - \frac{i_C}{i_L}\right]$

The above concept can be summarised graphically as shown in the Figure below, which represents, Evans diagram. In summary, activation polarization can occur in the anode and the cathode while concentration polarization is common at the cathode.



5. Since the process is dominantly ionic, Tafel equation can be written as,

$logi = logi_0 + \frac{\beta F \eta}{2.303RT}$

From the above, a plot of $logi$ versus η should be linear with slope equal to $\frac{\beta F}{2.303RT}$. Similarly, the intercept is equal to $logi_0$. Therefore,

$0.002 = logi_0$ indicating that $i_0 = 1.00\ V$.

Also, $\frac{\beta F}{2.303RT} = 0.5$, $\beta = \frac{0.5 \times 2.303 \times RT}{F} = \frac{0.5 \times 2.303 \times 8.314\ JK^{-1} \times 273\ K}{96500\ C} = 0.027$

(ii) Class Activity

(1) What are the significances of Butler-Volmer and Tafel equations (5 minutes)

(2) Sketch potentiodynamic polarization plots for a corrosion reaction and explain how the following parameters can be obtained from the plots (1) Corrosion potential (2) Corrosion current (3) Anodic Tafel constant (4) Cathodic Tafel constant. What are the significant of each of these parameters

5.0 Conclusion

The most interesting aspect of polarization is that what occurs in the cathode may not be exactly the same, at the anode. Therefore, anodic and cathodic polarization should first be considered separately and the total polarization is the some of the two. Evans diagram summarises what happened to total polarization. It is worth observing that polarization can be perfectly analysed graphically, once the data has been obtained.

6.0 Summary

This section summarises the chemistry behind the major types of polarization and supports them with appropriate modes. The section greatly bridges the gap between practical and theoretical aspect of polarization. It is indeed interesting to study this unit with understanding.

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Link to slide show:https://www.slideshare.net/GamryInstruments/echem-basics-for-users

MODULE 3

STUDY UNIT 1: MASS TRANSPORT

2.0 Introduction

2.0 Intended Learning Outcomes

3.0 Main Content

3.1 Transportation in electrochemical systems

3.11.1 Mass transport

3.1.2 Ion transport and conductivity

3.12 Ostwald dilution law

3.13 Ionic atmosphere and Onsager equation

3.14 The law of the independent migration of ions

3.15 Kohlrausch law

3.16 Ionic activity

3.17 Migration of ion in electrolyte

3.18 Determination of solubility by conductance measurements

3.19 Conductivity titrations

3.20 Electrolytic cell and electrolysis

3.21 Rotating disk electrode (RDE) theory: the Levich equation

4.0 (i) Self Assessment Exercise and Answers

(ii) Class Activity

5.0 Conclusion

6.0 Summary

7.0 References/Further Reading

1.0 Introduction

All transports (including mass transport) are based on the fact that the rate of change for a system physical property is a function of the spatial gradient of the property. Generally, the concept of transport involves the changing of a system property, in respond to a non-equilibrium distribution of the property. One of the fundamental requirements for transportation is that there should exist a spatial distribution of the system's property, that is different from that at equilibrium.

The quantity transferred through a given area in a given amount of time is called flux. Generally, when a spatial imbalance or gradient exist for a given property, flux will occur. Generally, for a given property, flux is defined as expressed in equation 5.1:

$$J = -k\frac{d(property)}{dx} \qquad 5.1$$

where J is the flux. The derivative represents the spatial gradient of the quantity of interest (for example, mass or energy). The negative sign indicates that the flux occurs in the opposite direction of the gradient, therefore flux will lead to the reduction in the gradient, if external force is not applied to maintain the gradient. In equation 58, the term k is called the transport coefficient.

2.0 Intended Learning Outcome

When you have studied this session, you should be able to:

i. Understand the concept of mass transport as it applies to electrochemistry
ii. Understand the concept of flux in mass transport
iii. Understand the three major types of mass transport in electrochemistry
iv. Understand the concept of rotating disc electrode and the derivation of Levich law
v. Understand the application of Levich equation in electrochemistry

3.0 Main Content

3.1 Transportation in electrochemical system

3.1.1 Mass transport

All transports (including mass transport) are based on the fact that the rate of change for a system physical property is a function of the spatial gradient of the property. Generally, the concept of transport involves the changing of a system property, in respond to a non-equilibrium distribution of the property. One of the fundamental requirements for transportation is that there should exist a spatial distribution of the system's property, that is different from that at equilibrium.

The quantity transferred through a given area in a given amount of time is called flux. Generally, when a spatial imbalance or gradient exist for a given property, flux will occur. Generally, for a given property, flux is defined according to the equation

$$J = -k\frac{d(property)}{dx} \qquad 5.2$$

where J is the flux. The derivative represents the spatial gradient of the quantity of interest (for example, mass or energy). The negative sign indicates that the flux occurs in the opposite direction of the gradient, therefore flux will lead to the reduction in the gradient, if external force is not applied to maintain the gradient. k is called the transport coefficient. Consider diffusion of a particle from the bulk electrolyte to the electrode, the diffusion gradient will be defined as the difference in concentration of the diffusing specie between the bulk and the

electrode, divided by the distant. The diffusion flux will be defined as the product of the diffusion coefficient and that of the diffusion gradient.

In electrochemistry, the most common and significant transport process is the mass transport. An electrode reaction proceeding at a finite rate involves movement of reacting materials between the electrode and the solution surrounding it. In the absence of fluid turbulence, ions are transferred from solution to an electrode by three principal mechanisms:

i. Migration: Movement of charge body under the influence of an electric field
ii. Diffusion: Movement of a specie under the influence of concentration gradient
iii. Convection: This results from Stirling or hydrodynamic transport

For a given species, the rate of transfer in the y-direction per unit area perpendicular to y at any point in the fluid, can be expressed according to equation 5.3

$$N_t = CU\frac{d\phi}{dx} - D\frac{\partial x}{\partial y} + VC \qquad 5.3$$

where N_t is the total rate of transfer, C is the concentration of a given specie, U is the mobility, ϕ is the potential, y is the distance in the direction of the transfer, D is the diffusion coefficient, V is the velocity of bulk fluid movement in the direction of the transfer. The first, second and third terms of equation 61 represent the contributions from migration, diffusion and convection respectively. In the bulk only the ions are engaged in the charge transport.

3.1.2 Ion transport and conductivity

Ion transports deals with the migration of cations towards the negatively charged electrode and anions towards the positively charged electrode. This migration of ion under applied electric field can be studied by measuring the electrical conductivities of the electrolyte solutions. The classical method of measuring the electrical conductivity of a solution of an electrolyte is connect the solution of the electrolyte as one of the resistant (r) in a Wheatstone bride assembly, as shown in Fig. 5.1

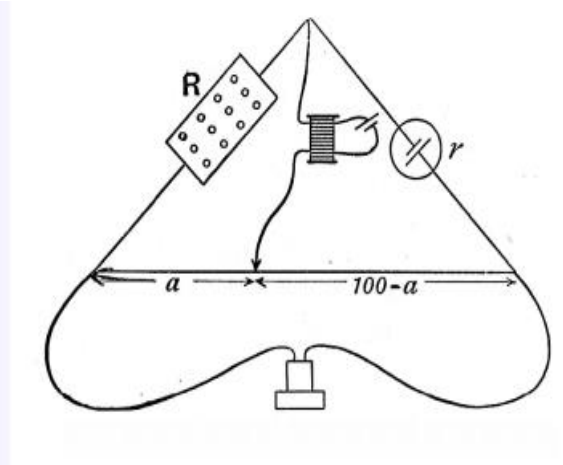


Fig. 5.1: Wheatstone bride assembly for measuring conductivity of an electrolyte

In the diagram, the resistant, r is that of the electrolyte while R is a known resistant. In this assembly, an alternating current (ac) is used because the use of direct (dc) current will initiate polarization and causes electrolysis. The balance point can be detected by using an ac detector (in this case, the balance point is achieved when the detector attained a zero reading) or a telephone (in this case the balance point is when the sound produced is minimal). Consider that the balance point is as indicated in the 100 cm meter rule, then the under listed formula is applicable,

$$\frac{R}{r} = \frac{a}{100-a} \qquad 5.4$$

Therefore, the resistance of the conductivity cell is given as,

$$r = \frac{R(10-a)}{a} \qquad 5.5$$

And its conductance, defined as the inverse of resistance, is given as,

$$Cond = \frac{1}{r} = \frac{a}{R(100-a)} \qquad 5.6$$

Generally, the higher the resistance, the lower the conductance. The unit of resistance is ohm while that of conductance is ohm^{-1} (and is given a special name, Siemens, denoted as S. (1 Ohm^{-1} = 1S). From Ohms law, the resistance of a sample is proportional to its length, l and inversely proportional to its cross sectional area, A. The constant of proportionality is called resistivity, ρ (which is an inverse of conductivity). Therefore, Ohms law can be expressed according to equation 5.7,

$$R = \rho\frac{l}{A} \qquad 5.7$$

Since, $\rho = \frac{RA}{l}$, the unit of conductivity is therefore, Sm^{-1}. However, it is unrealistic to calculate the conductivity of a solution of electrolyte from data obtained from measurement of length and cross-sectional area because current distribution in an electrolyte is complicated. Often, this challenge is overcome by using sample of known resistivity, k* (such as aqueous solution of KCl) to obtained a cell constant, G* and the resistance of the standard, R*. If the resistance of the electrolyte solution is R, then its conductivity will be given as k = G*/R. Technically, the solution whose conductivity is known is normally contained in a conductivity cell (see Fig. 5.2), whose cross-sectional area and length are known.

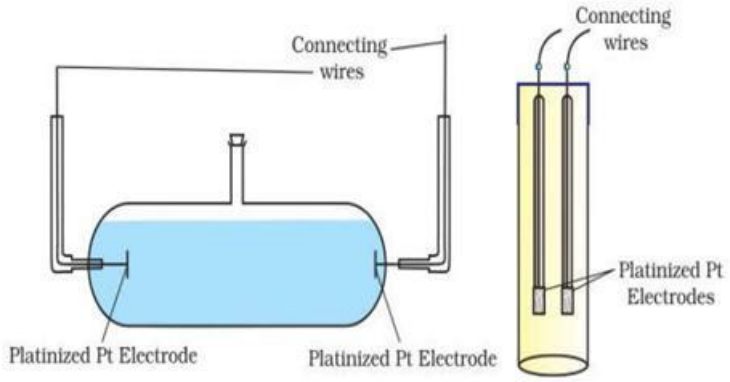


Fig. 5.2: Two different types of conductivity cell

As shown in the above diagrams, a typical conductivity cell consists of two platinum electrodes coated with platinum black. If the distance of separation is l and the cross-sectional area is A, then the resistance of the column of a solution in the cell is given by equation 5.7. The quantity, $\frac{l}{A}$ is called cell constant and can be written as,

$$R = \rho G^* = \frac{G^*}{k}$$

where k is the inverse of resistivity, i.e. conductivity. Consequently, $G^* = \frac{R}{\rho} = Rk$.

The conductivity of a solution depends on the number of ions present, the size and charge of the ions when they are dissociated, the concentration of the ion and the rate of migration of the ion under the influence of applied potential. Therefore, the term molar conductivity is often use to account for the dependent of conductivity on concentration. Molar conductivity is the conductivity per mole of the sample. Therefore, molar conductivity can be defined as, $\wedge_m = \frac{k}{C}$. C is the concentration of the electrolyte in mol/dm^3. The unit of $\wedge_m$ is Sm^{-1}mol^{-1}dm^{-3} or Scm^{-1}mol^{-1}dm^{-3}. It follows from the above that the molar conductivity of an electrolyte is expected to be independent on the concentration of the electrolyte. However, for two major reasons, the molar concentration of an electrolyte varies with concentration. Firstly, for weak electrolyte, there is no unique relation between conductivity and concentration and for strong electrolyte, the interaction of ions leading to the formation of ion pairs, may hinder the conductivity of the solution, since ion pair do not conduct electricity. Several studies on the variation of molar conductivity of an electrolyte with concentration have shown that there are two types of electrolyte, namely, weak and strong electrolyte. The molar conductivity of a strong electrolyte decreases slightly with concentration, while that of a weak electrolyte is normal at concentration close to zero but decreases sharply as the concentration increases.

Fig. 30 shows the variation of conductivity of HCl (strong electrolyte), CH_3COOH (a weak electrolyte) and their sodium salts (i.e. NaCl-strong electrolyte and CH_3COONa- a weak electrolyte). It is evident from the Figure that at a given concentration, the molar conductivity of a strong electrolyte is greater than the molar conductivity of a weak electrolyte because, most weak electrolyte shows partial ionization in solution while strong electrolytes ionizes almost completely in solution. It is also observed from the plots that conductivity increases with increase in concentration.

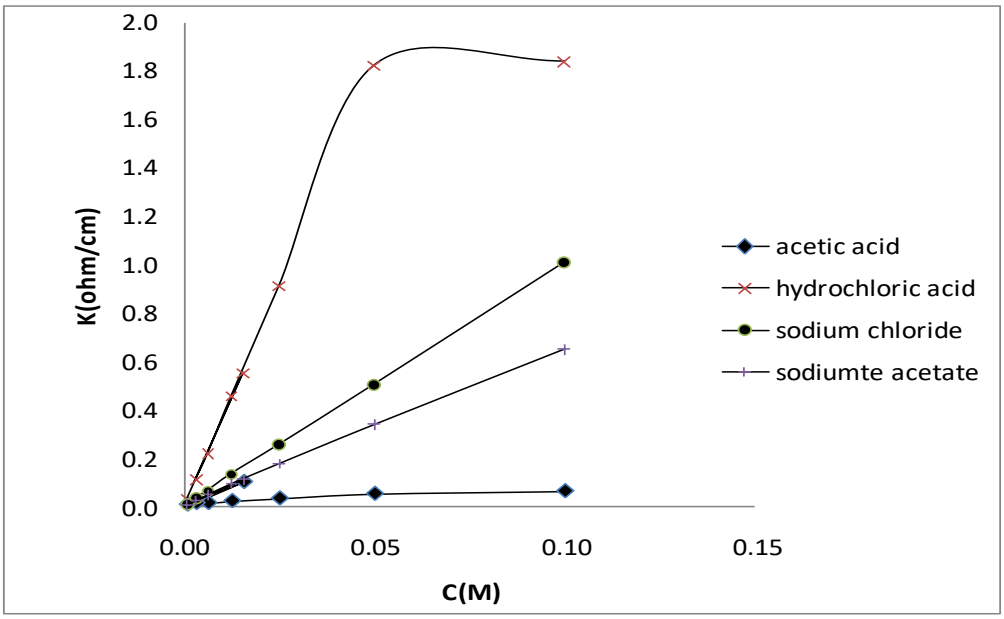


Fig. 5.3: Variation of conductivity of some electrolyte with concentration

3.2 Ostwald dilution law

Ostwald dilution law is applicable to weak electrolyte and can be derived by considering the dissociation of weak electrolyte. If a weak electrolyte ionizes in water, such that the degree of dissociation is given by α ($0 < \alpha \leq 1$), then the equation for the dissociation can be written as,

$$HA + H_2O \rightarrow H_3O^+ + A^-$$

If the initial concentration of HA is C, then at time, t = 0, the concentrations of H_3O^+ and A^- will be zero. But at equilibrium, concentration of HA will be (1- α)C while concentrations of H_3O^+ and A^- will each be equal to αC. The equilibrium constant for the above reaction is,

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{(\alpha C)(\alpha C)}{(1-\alpha)C} = \frac{\alpha^2 C}{1-\alpha} \qquad 5.8$$

At the limit of very low concentration, $C \rightarrow 0$, the limiting molar conductivity, Λ_0 (i.e, the molar conductivity at the limit of zero concentration) is related to the degree of dissociation,

according to the equation, $\alpha = \frac{\Lambda_c}{\Lambda_0}$. where Λ_c is the molar conductivity at concentration, C. From equation 5.8, we have,

$$1 - \alpha = \frac{\alpha^2 C}{K_a}$$

Dividing both sides of the above equation by α yields the following equation,

$$\frac{1}{\alpha} - \frac{\alpha}{\alpha} = \frac{\alpha^2 C}{\alpha K_a}$$

Therefore,

$$\frac{1}{\alpha} - 1 = \frac{\alpha C}{K_a}$$

$$\frac{1}{\alpha} = 1 + \frac{\alpha C}{K_a}$$

Substituting for $\alpha = \frac{\Lambda_c}{\Lambda_0}$, in the above expression leads to equation 5.9, after simplification,

$$\frac{1}{\frac{\Lambda_c}{\Lambda_0}} = 1 + \frac{\frac{\Lambda_c}{\Lambda_0} C}{K_a}$$

$$\frac{\Lambda_0}{\Lambda_c} = 1 + \frac{\Lambda_c}{\Lambda_0} \cdot \frac{C}{K_a} \qquad 5.9$$

Dividing both sides of equation 75a by Λ_0 gives the **Ostwald law** of dilution, which can be expressed as follows,

$$\frac{\mathbf{1}}{\Lambda_c} = \frac{\mathbf{1}}{\Lambda_0} + \frac{\Lambda_c}{(\Lambda_0)^2} \cdot \frac{C}{K_a} \qquad 5.10$$

From the Ostwald law, it is evident that a plot of $\frac{1}{\Lambda_c}$ versus $\Lambda_c C$ should be linear, with slope and intercept equal to $\frac{1}{K_a}(\Lambda_0)^2$ and $\frac{1}{\Lambda_0}$ respectively. Therefore, the application of the Ostwald dilution law can be used to estimate the values of the limiting molar conductivity and the acid constant. Fig. 31, shows a plot verifying Ostwald law for CH_3COOH.

Strong electrolyte shows deviation from the behaviour of weak electrolytes, which implies that Ostwald law may not be applicable. The deviation from ideal behaviour is due to electrical interactions between ions, which manifest as ionic atmosphere and asymmetry/relaxation effect. The basses of the interionic attractions are ascribed to the works of L. Onsager (1926) and those of P. Debye and E. Hückel (1932).

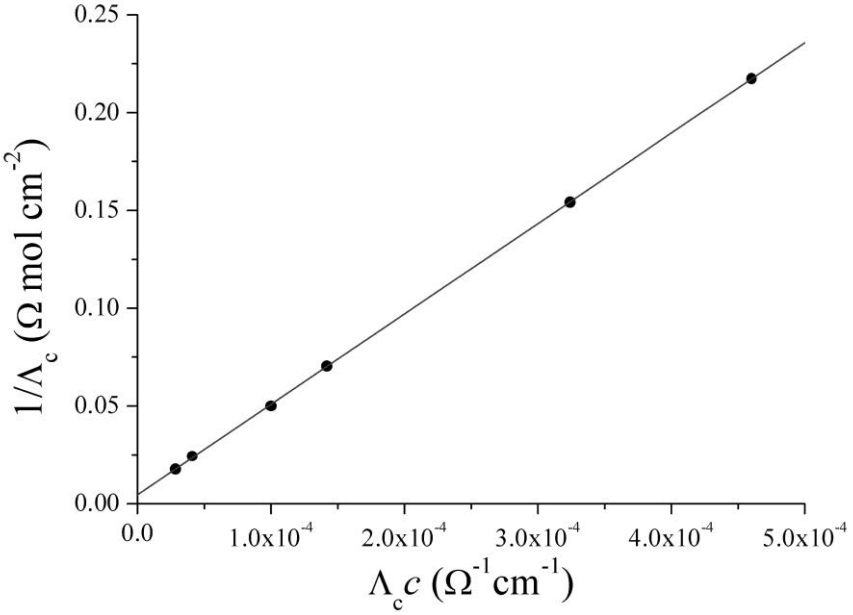
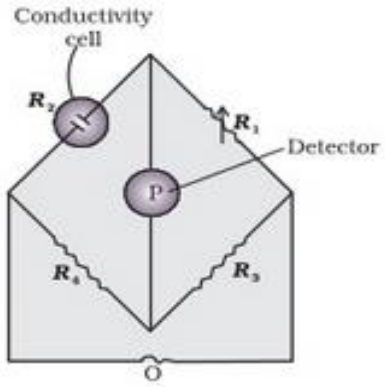


Fig. 5.4: Verification of Ostwald law for CH_3COOH

Worked example 1

The circuit presented below was used to measure the resistant of a conductivity cell. If the known resistance is, R_1 = 2.5 ohms, R_3 = 1.2 ohms and R_4 = 2 .0 ohm. Calculate the conductance of the conductivity cell



When the cell is balance, the resistances of the resistors will satisfy the following equation,

$$\frac{R_2}{R_1} = \frac{R_4}{R_3}$$

Therefore,

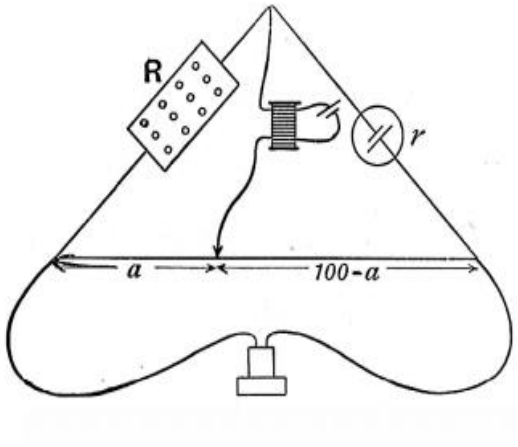
$$\frac{R_2}{2.5} = \frac{2}{1.2}$$

$$R_2 = \frac{5}{1.2} = 4.17$$

Conductance is the inverse of resistance, therefore, the conductance of the conductivity cell = $1/R_2 = 0.24\ ohm^{-1}$

Worked example 2

In an attempt to measure the conductance of a conductivity cell, a Wheatstone bridge (shown below) was used. The conductivity cell is designated as r while R is a resistor of capacity, 10 ohms. If the balance point was established when a = 40 cm. Calculate the resistance and the conductance of the conductivity cell.



When the circuit is balance, the following equation is applicable, $\frac{R}{r} = \frac{a}{100-a}$. Therefore,

$$\frac{10}{r} = \frac{40}{100-40}$$

$$\frac{10}{r} = \frac{40}{60}$$

$$r = \frac{600}{40} = 15\ ohm$$

Worked example 3

The resistance of a conductivity cell containing 0.1 mol/L KCl solution is 1000 ohms. The resistance of the same cell when filled with 0.02 mol/L KCl solution is 500 ohms. Calculate the conductivity and molar conductivity of 0.02 mol/L KCl solution. Given that the conductivity of 0.1 mol/L KCl solution is 1.29 S/m.

Solution

The cell constant = conductivity x resistance = 1.29 x 1000 = 1290 m^{-1} =12.90 cm^{-1}.

Conductivity of 0.02 mol/L = cell constant/resistance = 1290/500 = 2.58 S/m

Concentration = 0.02 x 1000 mol/m^3 = 20 mol/m^3.

Therefore, molar conductivity = conductivity/concentration = 2.58/20 = 0.129 Sm^2mol^{-1}

Worked example 4

A conductivity cell containing 0.01 mol/dm^3 KCl at 298 K has a resistance of 140 Ω. Similar concentration of HCl at the same temperature was found to has a resistance of 52 Ω. If the conductivity of the solution of KCl is 1.4 x 10 $^{-3}\Omega^{-1}$cm^{-1}, calculate the molar conductivity of HCl.

Solution

The cell constant is given as the product of the specific conductivity and the resistance. Hence the cell constant, G* is,

$$\boldsymbol{G^*} = (1.4 \times 10^{-3}\Omega^{-1}cm^{-1})(140\ \Omega) = 0.196\ \text{cm}^{-1}$$

Therefore, the specific conductivity of 0.01 mol/dm^3 of HCl will be given as

$$\boldsymbol{k_{(HCl)}} = \frac{G^*}{R} = \frac{0.196\ \text{cm}^{-1}}{52\ \Omega} = 3.77 \times 10^{-3}\Omega^{-1}cm^{-1}$$

The molar conductivity of HCl will be given as,

$$\boldsymbol{\Lambda_{(HCl)}} = \frac{k_{(HCl)}}{C} = \frac{3.77 \times 10^{-1}\Omega^{-1}m^{-1}}{0.01 \times 10^3\ molm^{-3}} = 3.77 \times 10^{-2}\Omega^{-1}m^2mol^{-1}$$

$$= 3.77 \times 10^{-2}\ Sm^2mol^{-1}$$

Worked example 5

The conductivity of aqueous solution of KCl (0.0005 mol/dm^3) at 298 K is 7.22 x 10^{-3} Sm^{-1} while that of the solvent (water) is 0.007 x 10^{-3} Sm^{-1}. Calculate the molar conductivity of KCl in the solution.

Solution

Specific conductivity is additive. Therefore,

$$\boldsymbol{k_{(solution)}} = k_{(KCl)} + k_{(H_2O)}$$

$$\boldsymbol{k_{(KCl)}} = k_{(solution)} - k_{(H_2O)} = (7.22 - 0.007)10^{-3}Sm^{-1} = 7.21 \times 10^{-3}Sm^{-1}$$

Therefore,

$$\boldsymbol{\Lambda_{(KCl)}} = \frac{k_{(KCl)}}{C} = \frac{7.21 \times 10^{-3}Sm^{-1}}{0.0005 \times 10^3 molm^{-3}} = 1.442 \times 10^{-2}Sm^2mol^{-1}$$

Worked example 6

The Table below, presents values of the molar conductivity of various concentrations of NaI at 298 K. Verify that the data obey Kohlrausch law and hence calculate the limiting molar conductivity.

$\Lambda_c\ (Sm^2mol^{-1})$	12.54	12.43	12.13	11.92	11.67
$\sqrt{C}\ (\text{mol/m}^3)^{\frac{1}{2}}$	0.50	1.00	2.336	3.162	4.472

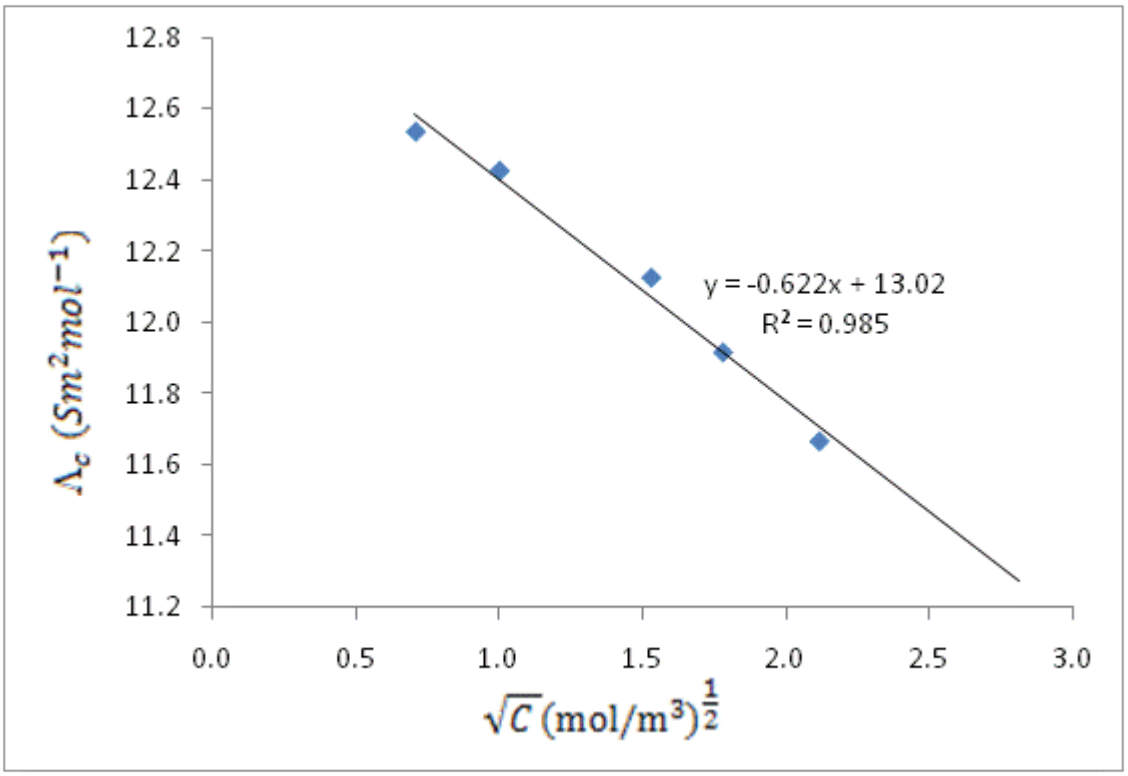
Solution

Kouhrash law can be expressed as, $\Lambda_c = \Lambda_0 - k\sqrt{C}$. This implies that a plot of Λ_c versus $\sqrt{C}$ should be linear with intercept equal to the limiting molar conductivity, Λ_0. The Table of values and the plots developed from th Kourash law are presented below

Table of values

Λ_c (Sm^2mol^{-1})	12.54	12.43	12.13	11.92	11.67
C (mol/m^3)	0.50	1.00	2.336	3.162	4.472
$\sqrt{C}$ $(\text{mol/m}^3)^{\frac{1}{2}}$	0.7071	1.0000	1.5284	1.7782	2.1147

From the plot, the equation for the straight line is y = -0.622x + 13.02. The plot is linear with R^2 value equal to 0.985. Therefore, the data obey Kohlrausch law and the limiting molar conductivity is 13.02 Sm^2mol^{-1}



Variation of molar conductivity of NaI with the square root of concentration.

Worked example 7

Values of the molar conductivity of various concentrations of ethanoic acid are presented in the Table below. Use appropriate model to estimate the values of the limiting molar conductivity and the dissociation constant of the acid.

Λ_c (Scm^2mol^{-1})	0	0.0004	0.0009	0.0025	0.010	0.040
C (mol/dm^3)	390.70	73.90	51.15	31.65	16.21	8.19

Solution

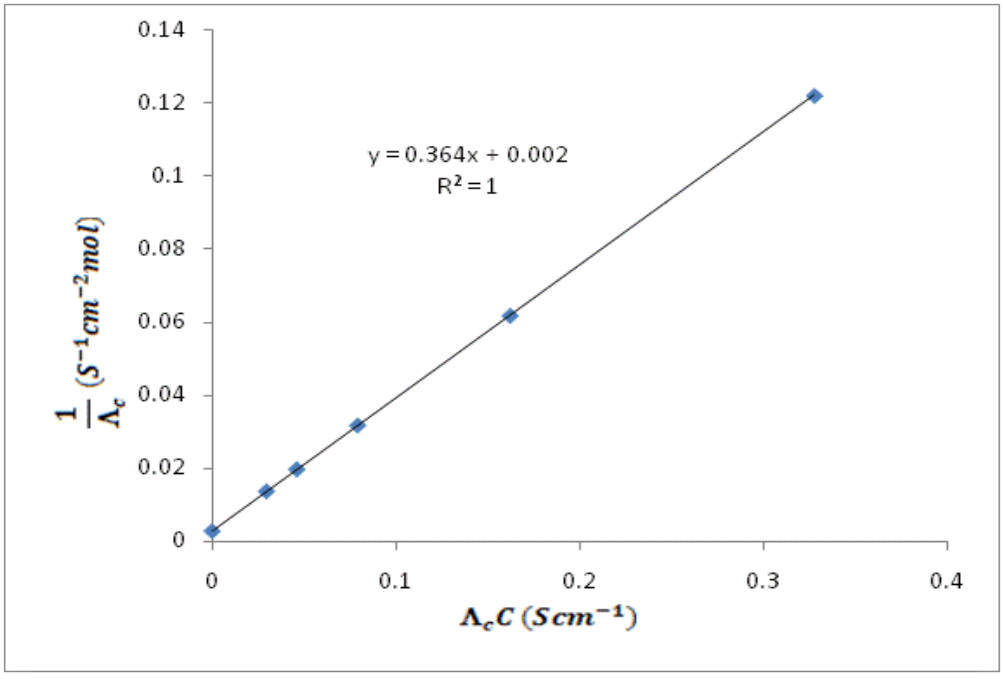
The Ostwald law of dilution can be expressed as follows,

$$\frac{\mathbf{1}}{\Lambda_c} = \frac{\mathbf{1}}{\Lambda_0} + \frac{\Lambda_c}{(\Lambda_0)^2}.\frac{\mathbf{C}}{\boldsymbol{K_a}}$$

From the Ostwald law, it is evident that a plot of $\frac{1}{\Lambda_c}$ versus $\Lambda_c C$ should be linear, with slope and intercept equal to $\frac{1}{K_a}(\Lambda_0)^2$ and $\frac{1}{\Lambda_0}$ respectively. Therefore, the application of the Ostwald dilution law can be used to estimate the values of the limiting molar conductivity and the acid constant. The Table of values and the plot are presented below,

Table of value

Λ_c (Scm^2mol^{-1})	C (mol/dm^3)	$\frac{1}{\Lambda_c}$ $(S^{-1}cm^{-2}mol)$	$\Lambda_c C$ (Scm^{-1})
390.7	0	0.00256	0
73.9	0.0004	0.013532	0.02956
51.15	0.0009	0.01955	0.046035
31.65	0.0025	0.031596	0.079125
16.21	0.01	0.06169	0.1621
8.19	0.04	0.1221	0.3276



Variation of $\frac{1}{\Lambda_c}$ with $\Lambda_c C$ for ethanoic acid

From the plot, the slope = 0.364, therefore, $\frac{1}{K_a}(\Lambda_0)^2$ = 0.364. Also, intercept = 0.002, therefore $\frac{1}{\Lambda_0}$ = 0.002. The value of the limiting molar conductivity, $\Lambda_0 = \frac{1}{0.002} = 500\ Scm^2mol^{-1}$. The dissociation constant can be derived as follows,

Since $\frac{1}{K_a}(\Lambda_0)^2 = = 0.364$,

$$K_a = \frac{(\Lambda_0)^2}{0.364} = \frac{(500\ Scm^2mol^{-1})(500\ Scm^2mol^{-1})}{0.364} = \quad 686813.2\ S^2cm^{42}mol^{-2}$$

3.3 Ionic atmosphere and Onsager equation

In solution of an electrolyte, each ion is surrounded by oppositely charged ions. In this case, the central ion exists, which could attract the electron cloud of the oppositely charged ions. Therefore, the central ion has an ionic atmosphere of oppositely charged ions, which has the potential of slowing down the velocity of ion. In the absence of electric field, the central ion may be symmetrically surrounded by the counter ions but when an electric field is applied, the central ion and the counter ion will adjust themselves and the arrangement will no longer be symmetry but asymmetry. This adjustment is provoked by the application of an electric field which will cause cations to move toward the cathode and anions toward the anode. The difference in charge between the central ion and its atmosphere will also cause electrostatic attraction between them hence the motion of the ions will be slowed. This effect on the speed of ion due to lack of symmetry (when an electric field is applied) resulting from the slowness of the ionic atmosphere to readjust itself is called **symmetry or relaxation effect**. On the other hand, **electrostatic or electrophoretic effect** (which occurs also during the electrophoretic motion of charged colloidal particles in an electric field) is due to the simultaneous movement of ions and their ionic atmosphere. In this case, the central ion moves in one direction, the counterions surrounding it move in the opposite direction. All ions, including the central one, carry some solvent along (their solvation shell), the net result being a slowdown of the central ion. This effect is equivalent to an increase in viscosity of the solvent or the moving ion and it strengthen the atmosphere to drag the ion with it.

For a univalent strong electrolyte, Onsager found that, incorporating the relaxation and electrophoretic effect, leads to a relation that reveals that the molar conductivity of a univalent strong electrolyte is proportional to the square root of the concentration

$$\Lambda_c = \Lambda_0 - \left[\frac{82.4}{(DT)^{\frac{1}{2}}\eta} + \frac{8.20\times10^5}{(DT)^{\frac{3}{2}}}.\Lambda_0\right]\sqrt{C} \qquad 5.11a$$

where D is the dielectric constant of the medium, T is the temperature and η is the coefficient of viscosity of the medium. The first term in the bracket (i.e. $\frac{82.4}{(DT)^{\frac{1}{2}}\eta}$) account for electrophoretic effect while the second term ($\frac{8.20\times10^5}{(DT)^{\frac{3}{2}}}$) account for relaxation effect. These terms are respective

constants and can be denoted as A and B respectively. Therefore, the Onsager equation can be written as,

$$\Lambda_c = \Lambda_0 - [A + B.\Lambda_0]\sqrt{C} \qquad 5.11b$$

3.4 The law of the independent migration of ions

Conductivity of an electrolyte can be considered to be the sum of the conductivity of the cation and that of the anion. For example, it has been found that for solution in the limit of zero concentration, where interionic interaction is negligible, the molar conductivity can be expressed as,

$$\Lambda_m^0 = F(z_+u_+v_+ + z_+u_-v_-) \qquad 5.12$$

where z is the charge of the ion, u is the ionic mobility, v_+ and v_- are the number of cation and anion per formula of the electrolyte. For example, in HCl, $v_+ = v_- = 1$. For $MgCl_2$, $v_+ = 1$ and $v_- = 2$ and for H_2SO_4, $v_+ = 2$ and $v_- = 1$. It should be noted that in the limit of zero concentration, ions are far apart and do not interact with each other. Therefore, the movement of cations and anions are totally independent because the presence of cations does not affect the movement of anions (and vice-versa). Simplification of equation 5.12 leads to **the law of the independent migration of ions**, which is expressed according to equation 5.13

$$\Lambda_c = v_+\Lambda_+ + v_-\Lambda_- \qquad 5.13$$

3.5 Kohlrausch law

Kohlrausch found that the conductivity of strong electrolytes varies with the square root of the concentration according to equation 5.14

$$\Lambda_c = \Lambda_0 - k\sqrt{C} \qquad 5.14$$

Therefore, Kohlrausch law reveals that the molar conductivity of a strong electrolyte is proportional to the square root of its concentration. Kohlrausch law laid the foundation for the development of Onsager equation, which was derived earlier. The fundamental similarity between Kohlrausch and Onsager laws is that a plot of Λ_c versus $\sqrt{C}$ is linear. The fundamental explanation of Kohraush constant, k (in equation 71) is that it represents contributions from relaxation and electrophoretic effects. i.e $k = [A + B.\Lambda_0]$. Fig. 5.5 shows plot for the variation of molar conductivity of KCl with the square root of its concentration. From the plot, it can be seen that Onsager and Kohlrausch laws are valid for the studied concentrations.

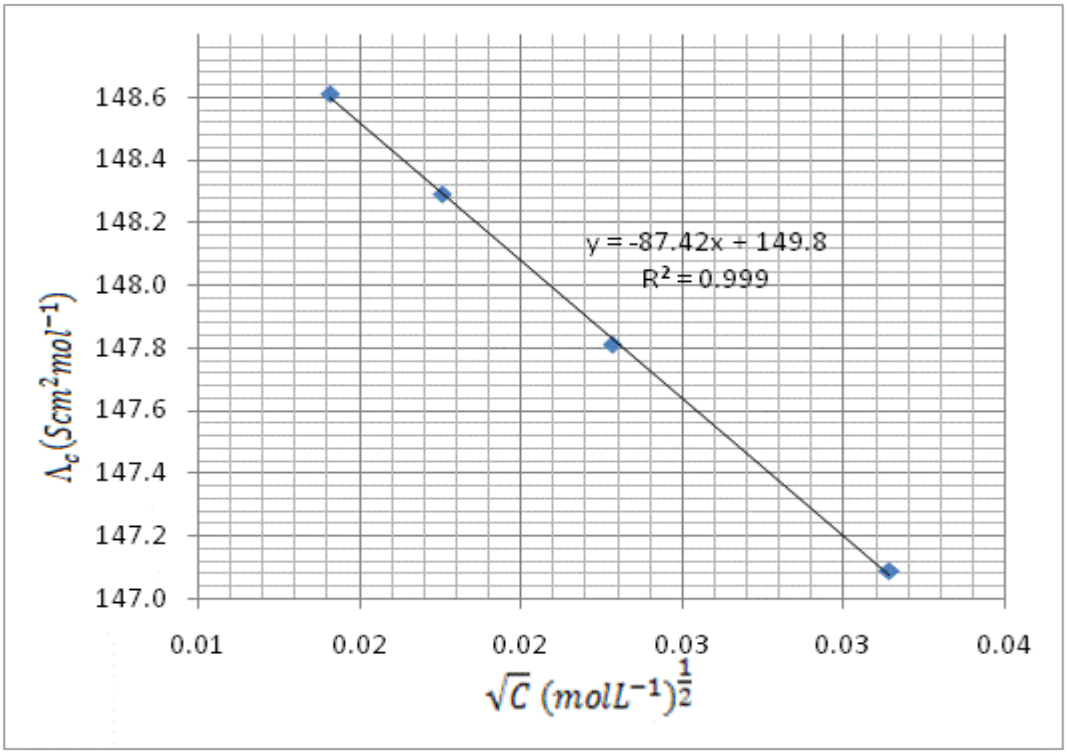


Fig. 5.5: variation of molar conductivity with square root of concentration for KCl

3.6 Ionic activity

It was G. N. Lewis, who found that experimental determined value of concentration of ions (and also molecules) in solution is often less than the actual concentration. This apparent value of concentration is called activity and is defined as the effective concentration of a molecule or ion in a solution. The ratio of the effective concentration to the actual concentration is called activity coefficient and can be expressed as,

$$\gamma = \frac{Effective\ concentration}{Actual\ concentration} = \frac{a}{C} \qquad 5.15$$

The concept of activity arises because in strong electrolytes, the formation of ion pairs reduces the strength of interaction between ions, thereby reducing the actual concentration of ions. From equation 725.15, activity is the product of the actual concentration and that of the activity coefficient. i.e. $a = \gamma C$. Activity coefficient depends on the composition of the solution, its molarity and on temperature. As the solution approaches ideality (i.e. obeying Henry's law) through the approach of zero concentration, the activity coefficient tends to unity. That is, $\gamma \rightarrow 1\ as\ C \rightarrow 0$.

Consider a 1: 1 electrolyte consisting of a cation, A^+ and an anion, A^-. The Gibb function of these ions can be written as follows,

$$G_{A^+} = G^0_{A^+} + RTlna_{A^+} \quad 5.16$$

$$G_{A^-} = G^0_{A^-} + RTlna_{A^-} \quad 5.17$$

The average Gibb function for the two ions can be written according to equation 5.18

$$\frac{G_{A^+} + G_{A^-}}{2} = \frac{G^0_{A^+} + G^0_{A^-}}{2} + \frac{RT}{2} ln(a_{A^+}a_{A^-}) \quad 5.18$$

Also, the mean Gibb function can be written as follows,

$$\frac{G_{A^+} + G_{A^-}}{2} = \frac{G^0_{A^+} + G^0_{A^-}}{2} + RT\ln(a_{\pm}) \quad 5.19$$

Comparing equation 5.18 with 5.19, gives the relationship for mean activity as follows,

$$a_{\pm} = (a_{A^+}a_{A^-})^{\frac{1}{2}} \quad 5.20$$

Since activity is related to the activity coefficient, i.e. $a = \gamma C$, we can also develop similar equation in terms of γ as follows,

$$\gamma_{\pm} = ([C_{A^+}\gamma_{A^+}][C_{A^-}\gamma_{A^-}])^{\frac{1}{2}} = (C_{A^+}C_{A^-})^{\frac{1}{2}}.(\gamma_{A^+}\gamma_{A^-})^{\frac{1}{2}}$$

However, activity coefficient takes care of concentration hence the above equation can be written as equation 5.21,

$$\gamma_{\pm} = (\gamma_{A^+}\gamma_{A^-})^{\frac{1}{2}} \quad 5.21$$

Generally for a salt represented as A_xB_y,, which dissolves to give a solution of x cation and y anion, the mean activity coefficient can be written according to equation 5.22

$$\gamma_{\pm} = (\gamma_+^x\gamma_-^y)^{\frac{1}{s}} \quad 5.22$$

where s = x + y. Through consideration of the effect of ionic atmosphere in lowering the energy of an ion as a result of columbic interaction with its ionic atmosphere, Peter Debye and Erich Huckel (1923) developed a model called Debye-Hückel theory. They explained that the lowering of the energy can be considered as the differences between the Gibb function and the ideal Gibb function of the solution. They concluded that at very low concentration, the activity coefficient can be calculated from the Debye-Hückel limiting law, which can be expressed as follow (equation 5.2),

$$log\gamma_{\pm} = -A|z_+z_-|I^{\frac{1}{2}} \quad 5.23$$

where A = 0.509 $(molkg^{-1})^{0.5}$ for an aqueous solution at 298 K. A is a function of relative permittivity and temperature. I is the ionic strength of the solution. Given a charge, i, the ionic strength of a solution is defined according to equation 5.44,

$$I = \frac{1}{2}\sum_i z_i^2 C_i \quad 5.44$$

When the ionic strength of the solution is too high, the limiting law (equation 80) will not be valid and the activity coefficient can be estimated from the extended Debye-Hückel theory (equation 5.25),

$$log\gamma_{\pm} = -\frac{A|z_{+}z_{-}|I^{\frac{1}{2}}}{1+BI^{\frac{1}{2}}} \qquad 5.25$$

where B is a constant which represents a measure of the closest approach of the ions

3.7 Migration of ion in electrolyte

At the anode, there is excess of positive ions arising from build-up of positive charges. Similarly, at the cathode, there is a build-up of negative charges, leading to excess of negative charges. The building up of ions leads to ionic migration. In this case, positive charge moves from the anode to the cathode while negative charge moves from the cathode o the anode. The process where positive charges move to the cathode and negative charges to the anode, under the influence of applied electric field is called ion migration. The fractions of current carried by the positive and negative ions are given by their transport numbers (i.e., $t_- + t_+$). Each mole of current that is passed through an electrochemical cell correspond to 1 mole of electrochemical change at each electrode, which indicate that the amount of ions transported in the electrolyte is also equal to 1 mole (i.e. $t_- + t_+ = 1$). The transport numbers of ions is strongly influenced by the conductance of an electrolyte, which can be expressed as follow,

$$L = \frac{kA}{l} \qquad 5.26$$

where L is the conductance in Siemens (S), k is the conductivity in S/cm, A is the surface area of the electrode in cm^2 and l is the thickness or length of electrolyte matrix in cm.

It has been found that the conductivity of a electrolyte is proportional to the following parameters,

i. The mobility of the ion
ii. The concentration of the ion
iii. Charge of the ion.

Mobility is defined as the limiting velocity of ion in an electric field of unit strength. Therefore, if the strength of an electric field is E, then the force exerted is given by

$$F = eEz = \frac{ze\Delta\phi}{L} \qquad 5.27$$

where e is the electronic charge, z is the charge of the ion and $\Delta\phi$ is the potential difference between two electrodes separated by a distance, L. However, in electrochemical system, ions in motions experience an opposing frictional force, which can be expressed according to Stokes law:

$$F_{fric} = 6\pi\eta r v \quad 5.28$$

whereη is the viscosity of the electrolyte, r is the radius of the ion and v is the velocity of the ion in solution (i.e. drift speed)? A system of this type attains a terminal velocity when the accelerating (equation 5.59) and the retarding forces (equation 5.60) counterbalance each other. Therefore,

$$6\pi\eta r v = eEz$$

$$v = \frac{eEz}{6\pi\eta r}$$

This terminal velocity is termed the mobility (u) defined as $u = \frac{v}{E}$. Therefore

$$u = \frac{ze}{6\pi\eta} \quad 5.29$$

The molar conductivity of an electrolyte is defined as, $\lambda = zuF$and for cation and anion, the molar conductivities are given by equation 5.30 and 5.31 respectively,

$$\lambda_+ = z_+ F u_+ \quad 5.30$$

$$\lambda_- = z_- F u_- \quad 5.31$$

where F is the Faraday's constant. On the other hand, the specific conductivity or conductance of an electrolyte is defined according to equation 5.32

$$k = Fzuvc \quad 5.32$$

where v is the number of cation or anion per formula unit of the electrolyte. Transport number of cation or anion can then be expressed as the ratio of the contribution made by the cation or anion to the total current carried in solution. Thus,

$$t_+ = \frac{z_+ u_+ C_+}{\Sigma z_i C_i u_i} \quad 5.33$$

$$t_- = \frac{z_- u_- C_-}{\Sigma z_i C_i u_i} \quad 5.34$$

3.8 Determination of solubility by conductance measurements

Let S be the solubility (in mole/L) of a sparingly soluble salt and k, the specific conductivity of the saturated solution, It can be shown that the solubility is related to the molar conductivity according to the following equation,

$$\Lambda_c = \frac{1000k}{S} \quad 5.35$$

Since the salt is sparingly soluble and the saturated solution is highly diluted, then it is expected that the $\Lambda_c \approx \Lambda_0$. Therefore, equation 5.35 can also be written as,

$$\Lambda_0 = \frac{1000k}{S} \quad 5.36$$

Hence, $S = \frac{1000k}{\Lambda_0}$. k can easily be determined experimentally but Λ_0 can be derived from ion conductivities data. Therefore, the solubility of a sparingly soluble salt can easily be estimated.

3.9 Conductivity titrations

Conductivity titration rely on measuring the conductivity of the titrant-titrant mixture as the titration continues. It has been widely used for the determination of the end point during the titration of various strengths of acid and base. For example, when a solution of a strong acid, e.g. HCl, is gradually neutralized by a strong base, e.g., NaOH, the protons of the strong acid are replaced by metal ions (Na^+), which have a much lower conductivity. The conductivity will therefore *decrease* steadily as the base is added. When neutralization is complete, further addition of the base does not remove any more ions, but instead will *bring* more ions, and thus the conductivity will start to increase. The conductivity changes with equivalents of base added will have a minimum at the **equivalent point** (or **end point**), when the acid is neutralized. In practice, the neutralization point is determined from the intersection of the two straight lines that give the conductivity in the regions with excess of acid and excess of base as shown in Fig. 5.6.

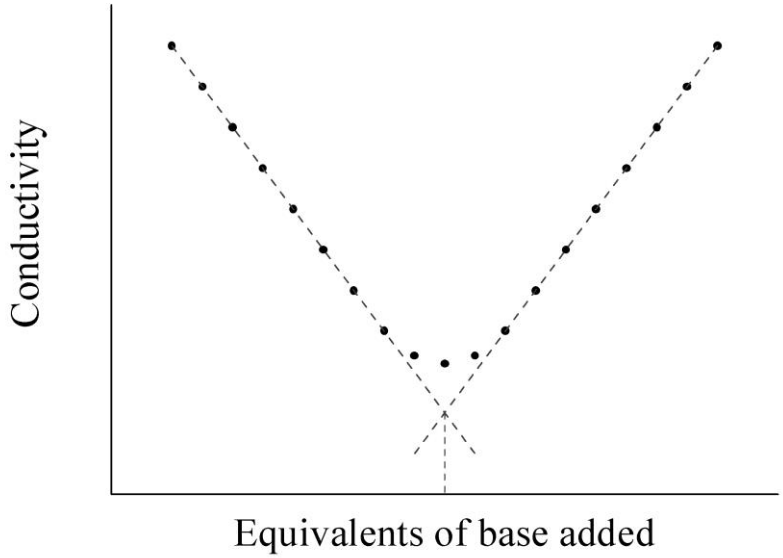


Fig 5.6: A typical pattern of plot for conductivity titration

If the acid is moderately weak or very weak, the conductivity curve shows a different shape, depending on the relative strength of the acid. If the acid is moderately weak (such as CH_3COOH), the salt formed during the neutralization usually dissociates better than the free acid, and after a small decrease, an increase is observed again. After the neutralization, the

conductivity increases again, but with a different slope. If the acid is very weak (such as boric acid or phenol), the conductivity increases steadily, but again with a different slope after neutralization. In this case it is better to titrate the very weak acid with a weak base, for which, due to its low conductivity, a (almost) constant conductivity is reached after neutralization.

Conductivity titrations have some significant applications including its uses in ion chromatography detector and for titration where low amount of ionic substances is involved. Conductivity titration is also useful in precipitation titration. For example, in the titration of $AgNO_3$ with NaCl, the product, AgCl and $NaNO_3$ are sparingly soluble, indicating that the conductivity of the mixture will remain fairly constant. However, when the end point is reached, the conductivity will increase.

3.10 Electrolytic cell and electrolysis

Electrolysis is the chemical decomposition of a compound or its molten form brought about by the passage of electricity through it. The compound or the molten form is called an electrolyte. An electrolyte is either dissolve in a solution or is present in a molten state. However, an electrolyte must be able to form ions. An electrode is usually a metal immersed in the electrolyte through which current enters or leaves the cell. An electrode where oxidation takes place (i.e. having deficient of electron) is a positive electrode called the anode while the negative electrode through which reduction occurs (having excess of electron) is called the cathode.

Electrolysis has a wider range of laboratory and industrial application. For example, in Fig. 5.7, an electrolytic assembly for the purification of copper is shown.

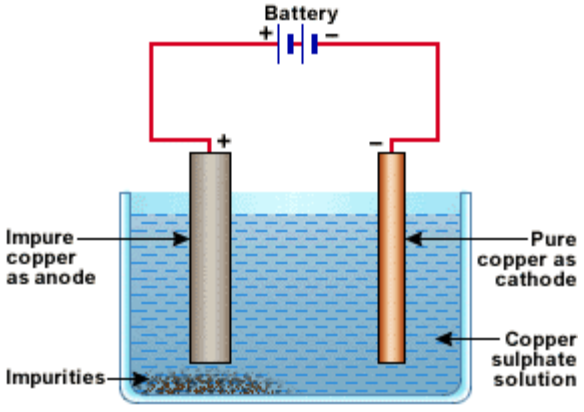


Fig. 5.7: Electrolytic assembly for the refining of copper

In this case, the impure copper is made the anode indicating that oxidation will take place according to the following equation,

$$Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e^{-}$$

Therefore, at the anode, the impure copper ionizes to produce copper ions, which migrate to the cathode and become deposited the according to the following equation,

$$Cu^{2+}_{(aq)} \; + \; 2e^{-} \; \rightarrow \; Cu_{(s)}$$

Therefore, impure copper is dissolved (oxidized) at the anode and become deposited (reduced) at the cathode.

Fig. 35, shows an assembly for the electrolysis of molten sodium chloride. In this case, the electrodes are not made from sodium but the cathode is a steel metal while the anode is a carbon electrode.

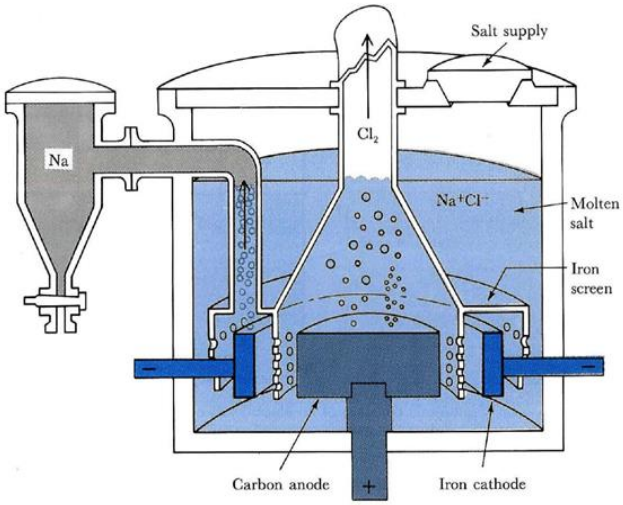


Fig. 5.8: Assembly for electrolysis of molten sodium chloride

During the electrolysis, sodium ions migrate to the cathode, where electrons enter the melt and reduce them to molten sodium metal according to the following equation,

$$Na^{+}_{(aq)} \; + \; e^{-} \; \rightarrow \; Na$$

At the anode, chloride ions migrate to the anode, lose their electron and become converted to chlorine gas,

$$Cl^{-} \; \rightarrow \; \frac{1}{2}Cl_{2(g)} + \; e^{-}$$

The overall reaction is given as,

$$NaCl_{(s)} \; \rightarrow \; Na_{(s)} \; + \; \frac{1}{2}Cl_{2(G)}$$

The product of electrolysis of aqueous NaCl is quite different from that of electrolysis of molten NaCl. The products of electrolysis of aqueous NaCl are NaOH, Cl_2 and H_2. This means the ions involved are H^+, Na^+, Cl^- and OH^- and the solvent is water. At the cathode, there is competition between the discharge of Na and hydrogen. The reactions can be written as,

$$Na^{+}_{(aq)} \; + \; e^{-} \rightarrow Na_{(s)} E^{0}_{cell} \; = \; -2.71\,V$$

$$H^+_{(aq)} \ + \ e^- \rightarrow \frac{1}{2}H_{2(g)} E^0_{cell} \ = \ 0.00\,V$$

Since the standard electrode potential required for the liberation of hydrogen gas is higher than that required for the liberation of molten sodium, the hydrogen gas will be liberated at the cathode. However, hydrogen is produced by the dissociation reaction of water according to the reaction,

$$H_2O \rightarrow H^+_{(aq)} \quad + \quad OH^-_{(aq)}$$

The net reaction at the cathode is the sum of the following half reactions,

$$H^+_{(aq)} \ + \ e^- \rightarrow \frac{1}{2}H_{2(g)}$$

$$H_2O_{(l)} \rightarrow H^+_{(aq)} \quad + \quad OH^-_{(aq)}$$

$$\boldsymbol{Net\ reaction}: \ \boldsymbol{H_2O_{(l)}} \ + \ \boldsymbol{e^-} \rightarrow \boldsymbol{\frac{1}{2}H_{2(g)}} \ + \ \boldsymbol{OH^-_{(aq)}}$$

At the anode, the following oxidation reactions are possible,

$$Cl^-_{(aq)} \quad \rightarrow \quad \frac{1}{2}Cl_{2(g)} \ + \ e^- E^0_{cell} \ = \ 1.36\,V$$

$$2H_2O_{(l)} \quad \rightarrow \ O_{2(g)} \ + \ 4H^+_{(aq)} \ + \ 4e^- E^0_{cell} \ = \ 1.23\,V$$

From the above reactions, water should be preferentially be oxidized because lower potential is required for its oxidation. However, because of the high overpotential of oxygen, chlorine gas is preferentially discharged at the anode through oxidation of chloride ion. In summary, the major reaction for the electrolysis of aqueous NaCl are

$$NaCl_{(aq)} \xrightarrow{H_2O} Na^+_{(aq)} \ + \quad Cl^-_{(aq)}$$

$$\boldsymbol{Cathode}: H_2O_{(l)} \ + \ e^- \rightarrow \frac{1}{2}H_{2(g)} \ + \quad OH^-_{(aq)}$$

$$\boldsymbol{Anode} \quad : \ Cl^-_{(aq)} \quad \rightarrow \quad \frac{1}{2}Cl_{2(g)} \ + \ e^-$$

$$\boldsymbol{Overall\ reaction}: \ \boldsymbol{NaCl_{(aq)}} \ + \ \boldsymbol{H_2O_{(l)}} \rightarrow \ \boldsymbol{Na^+_{(aq)}} + \boldsymbol{\frac{1}{2}H_{2(g)}} \ + \quad \boldsymbol{OH^-_{(aq)}} \ + \ \boldsymbol{\frac{1}{2}Cl_{2(g)}}$$

Fig. 5.9 show a schematic diagram for the electrolytic production of aluminium from its ore (aluminium oxide). The cost of converting this ore is expensive because its melting point is about 2000 °C. In other to overcome this challenge, the aluminium oxide is mixed with cryolite in order to reduce its melting point. In this case, the anode and the cathode are made from graphite. The molten aluminium is obtained at the bottom of the cell (negative electrode). The following reactions takes place at the cathode,

$$Al^{3+}_{(s)} \quad + \quad 3e^- \quad \rightarrow \quad Al_{(molten)}$$

At the anode, the following reaction takes place,

$$2O^{-2} \rightarrow 2O_{2(g)} + 4e^{-}$$

The overall reaction maybe written as,

$$2Al_2^{3+}O_3^{2-} \rightarrow 4Al_{(l)} + 3O_{2(g)}$$

One of the major problems with this extraction process is that the produced oxygen normally reacts with the graphite electrode (which serves as the anode) to form carbon (IV) oxide. Therefore, the anode is gradually worn off with time and need continuous replacement.

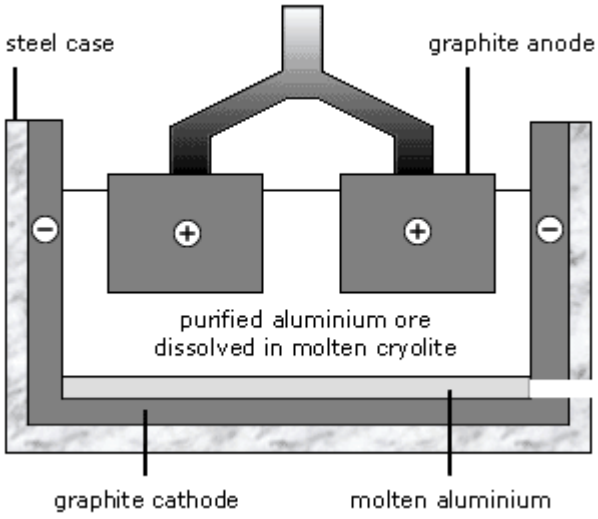


Fig. 5.9: Scheme for the production of aluminium by electrolysis

3.10.1 Laws of electrolysis

The fundamental laws of electrolysis were formulated by Michael Faraday between 1833 and 1934. There are two major laws of electrolysis and they are termed Faraday first and second laws respectively.

Faraday First law: The amount of chemical reaction which occurs at any electrode during electrolysis is proportional to the quantity of electricity passed through the electrolyte.

Faraday second law: The amount of different substances liberated by the passage of the same quantity of electricity through the electrolyte is proportional to the equivalent weight of the metal (i.e. atomic weight divided by number of electrons required to liberate the metal).

The quantity of electricity passing through an electrochemical system is given by the product of the current and time. That is Q = It. The unit of current is Ampere (A) and the unit of time is second (s). Therefore, the unit of the quantity of electricity is As, which is given a special name, called Coulomb. The amount of electricity requires to initiate and complete a given

electrochemical oxidation or reduction depends on the stoichiometry of the reaction, hence on the number of electrons associated with such reaction. The charge of an electron is 1.6021 x 10^{-19} Coulomb. Since Avogadro's number is 6.022 x 10^{23}, the quantity of electricity associated with one mole of electron is given as,

$$(1.6021 \times 10^{-19}C)(6.02 \times 10^{23}mol^{-1}) = 96487\ Cmol^{-1}$$

3.10.2 Some electrochemical cells or batteries

Primary cell

One of the significant differences between primary and secondary batteries is that a primary cell cannot be recharged with any efficiency, so the amount of energy it can deliver is limited to what the reactants that were placed in during its production stage. A secondary or storage battery is capable of being recharged; its electrode reactions can proceed in either direction. During charging, electrical work is required to provide the free energy needed to force the reaction in the non-spontaneous direction.

The principles of Georges Leclanche (1866) form the bases for modern dry cell. The electrolyte is a wet paste containing NH_4Cl to supply the hydrogen ions (see Fig. 5.9) The electrode reactions are

$$Zn_{(s)} \rightarrow Zn^{2+}_{(s)} + 2e^-$$

$$2MnO_2 + 2H^+ + 2e^- \rightarrow Mn_2O_3 + H_2O$$

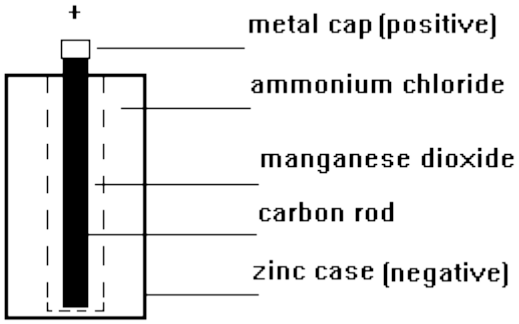


Fig. 5.9: Diagram of a primary cell (Leclanche dry cell)

Alkaline Battery

Alkaline battery was introduced in 1949.The cell consisted of KOH electrolyte, zinc-powder anode and MnO_2 as cathode (Fig. 5.10). These components enable the cell to produce higher currents and overcomes the corrosive effects of the acidic ammonium ion on the zinc. The cell reactions are,

$$At\ t\square e\ cat\square ode: Zn(OH)_2 + 2e^- \rightarrow Zn + 2OH^-$$

$$At\ the\ anode:\ \ Mn_2O_3\ +\ \ 2OH^- \rightarrow 2MnO_2\ +\ H_2O\ +\ 2e^-$$

The lead acid storage cell

The lead-acid storage cell is commonly used in automobiles and stationary engines (Fig. 5.11). The cell was invented by Gaston Planté in 1859 The conventional notation for this cell is,

$Pb_{(s)}$ | PbSO4(s) | $H_2SO_{4(aq)}$ || $PbSO_{4(s)}$, $PbO_{2(s)}$ | $Pb_{(s)}$

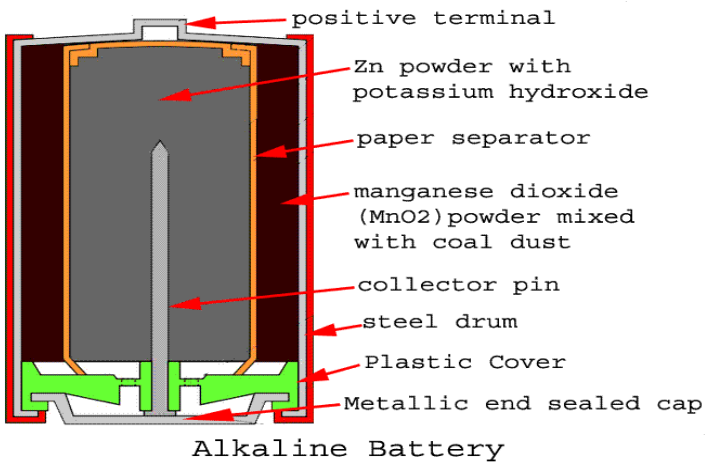


Fig. 5.10: Diagram of an alkaline battery

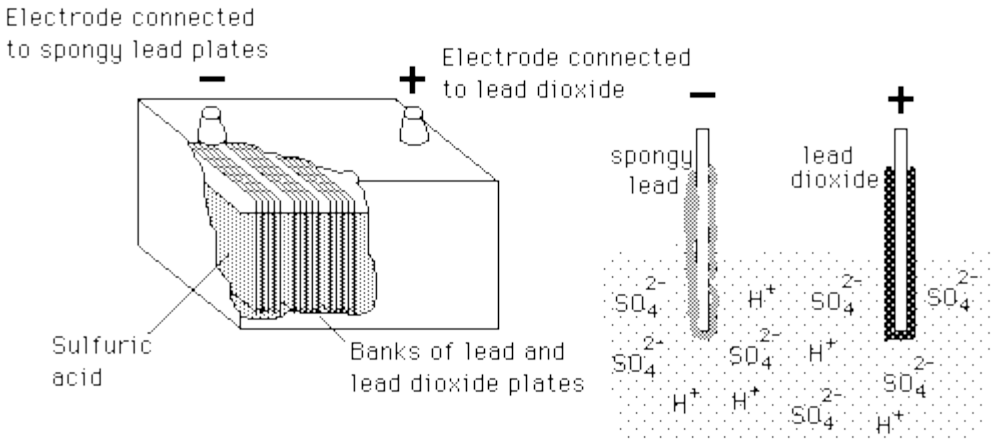


Fig. 5.11: Diagram showing the organization of a typical lead acid battery

The half-cell reactions for the lead acid battery are

$$At the cathode: PbO_2\ +\ 2e^- + 4H^+\ +\ SO_4^{2-} \rightarrow PbSO_4\ +\ 2H_2O E^0\ =\ 1.685\,V$$

$$At the anode:\ Pb\ +\ SO_4^{2-} \rightarrow PbSO_4\ +\ 2e^- E^0\ =\ -0.356\,V$$

$$Net reaction: Pb + PbO_2 +\ 2H_2SO_4 \rightarrow PbSO_4\ +\ 2H_2O E^0\ =\ 2.041\,V$$

In lead acid battery, the cell reaction gets to the right when it is discharging and to the left when it is charging. Two basic factors can limit the cell performance. These are in ability of $PbSO_4$

to be converted to PbO_2 and the inhibition of the flow of ions at low temperature as the electrolyte (H_2SO_4) becomes more viscous, especially when it is not charged.

Fuel cell

The birth of fuel cell dated back to 1839, when Sir William Grove first demonstrated the principle of its operation, which involves the following electrochemical reactions,

$$Atthecathode: \frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2OE^0 = 1.23\,V$$

$$Attheanode: H_{2(g)} \rightarrow 2H^+ + 2e^- E^0 = 0.00\,V$$

$$Netreaction: H_{2(g)} + \frac{1}{2}O_2 \rightarrow 2H_2OE^0 = 1.23\,V$$

However, the first working hydrogen-oxygen fuel cell (Fig. 5.12) was developed by Francis Thomas Bacon in England in 1959. Francis fuel cell used alkaline electrolyte (Fig. 5.13). In recent times there are fuel cells that user alcohols, hydrocarbon liquids, and even coal slurries as fuel. Much hope has been vested in methanol fuel cell, which operates through the following electrochemical reactions

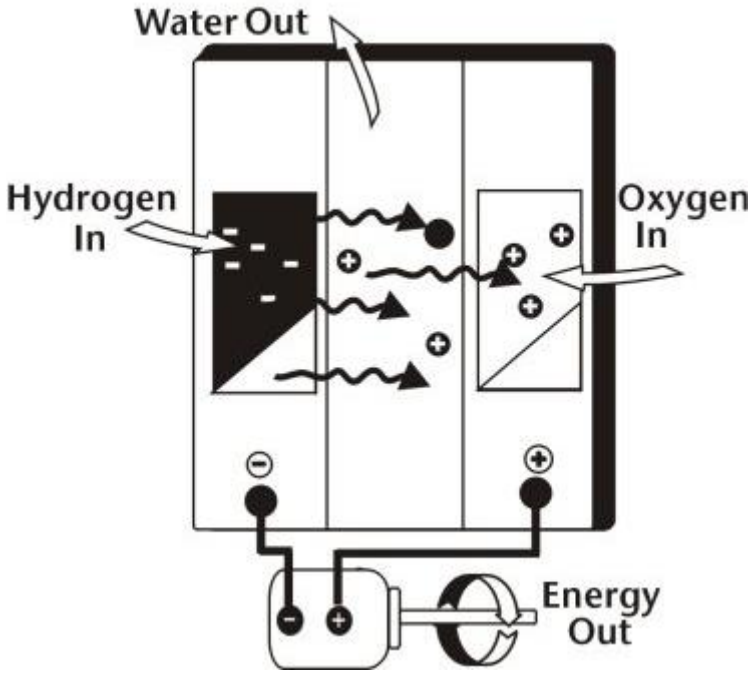


Fig. 5.12: Diagram of hydrogen-oxygen fuel cell

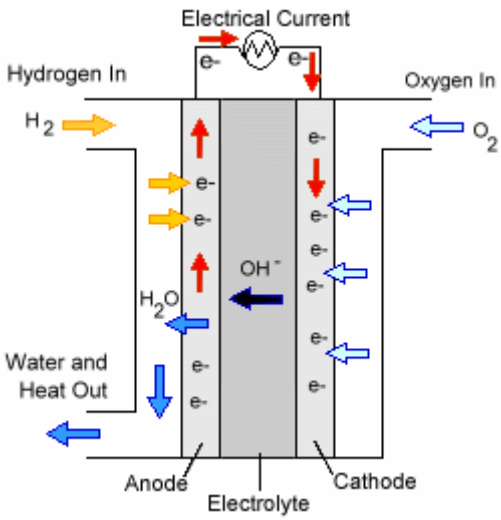


Fig. 5.13: Diagram of alkaline fuel cell

$$Atthecathode: \frac{1}{2}O_2 + 2H_2O + 2e^- \rightarrow 2OH^- E^0 = 1.23\,V$$

$$Attheanode: H_{2(g)} + 2OH^- \rightarrow 2H_2O + 2e^- E^0 = 0.00\,V$$

$$Netreaction: H_{2(g)} + \frac{1}{2}O_2 \rightarrow 2H_2O E^0 = 1.23\,V$$

Common electrolytes are sodium hydroxide, phosphoric acid or solid oxides. The major advantage of fuel cell is that it is eco-friendly because it does not produce environmental pollutant. However, fuel cells have some inherent setbacks. The output current can be very small because the rate of electrode reaction can become a limiting factor. Although coating the electrode with a suitable catalyst can improve the output current, it is relatively expensive to adopt this measure.

Worked example 8

(a) Calculate the mass of lead deposited at the cathode during electrolysis when a current of 2.50A flows through molten lead (II) bromide for 20.0min. (*A*r value: [Pb] = 207; *F* = 96500Cmol^{-1})

(b) Calculate the volume of oxygen produced at room temperature and pressure (rtp). when a concentrated aqueous solution of sulfuric acid, H_2SO_4, is electrolysed for 40 minutes using a current of 1.50A. (*F* = 96500 C.mol; 1 mole of gas occupies 24.4dm^3 at rtp)

(c) A student passed a constant electric current of 0.15A through a solution of silver nitrate, using pure silver electrodes, for 45min exactly. The mass of the anode decreased by 0.45g. Use this data to calculate the charge on a mole of electrons Hence the Avogadro's number. [Ag] = 108)

Solution

(a) The equation for the reaction can be written as,

$$Pb^{2+}_{(aq)} + 2e^- \rightarrow Pb_{(s)}$$

From the equation, 2F = 2 x 96500 C/mol of electricity is required for 1 mole of Pb (i.e. 207 g/mol) to be deposited. Quantity of electricity applied = It = 2.5 x 20 x 60 = 3000 C.

Therefore,

193 000 C/mol (i.e. 2F) deposits 207 g/mol of Pb

3000 C deposits $\frac{3000}{193000} \times 207\ g/mol\ of\ Pb = 3.22\ g\ of\ Pb$

(b) The equation for the reaction is $4OH^-_{(aq)} \rightarrow 2H_2O_{(l)} + O_{2)g)} + 4e^-$

From the equation, 4F (i.e. 4 x 96500 C/mol = 386000 C/mol) liberates 1 mole of oxygen gas (22.4 dm^3)

Quantity of electricity passed through the cell is Q = It = 1.5 x 40 x 60 = 3600 C

Therefore,

386000 C liberates 22. 4 dm^3 of oxygen gas

3600 C liberates $\frac{3600\ C}{386000C} \times 22.4\ dm^3 = 0.2089\ dm^3$

(c) The equation for the reaction is $Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$

The quantity of electricity passed through the cell, Q = It = 0.15 x 45 x 60 = 405 C.

Therefore,

0.45 g of Ag is deposited by 405 C of electricity

108 g of Ag (i.e. 1 mole of Ag) will be deposited by $\frac{108\ g}{0.45\ g} \times 405\ C = 97200\ C$

The equation for the reaction shows that 1 mole of electron is required to deposit one mole of Ag. Therefore, charge on one mole of electron = $\frac{108\ g}{0.45\ g} \times 405 \frac{C}{1} = 97200\ C$

The charge of one electron = 1.60 x 10^{-19} C/mol. Therefore,

$$N = \frac{97200\ C}{1.60 \times 10^{-19} C/mol} = 6.08 \times 10^{23} mol^{-1}$$

3.11 Rotating disk electrode (RDE) theory: the Levich equation

The general theory describing the rotating disk electrode was originally developed by Dr. Benjamin Levich in his landmark book called physicochemical hydrodynamics (Prentice-Hall). In 1962, this book was translated from Russian to English, and researchers in the United States and the United Kingdom rapidly built upon Dr. Levich's seminal work. Dr. Stanley Bruckenstein's laboratory at the University of Minnesota (and later at the University of Buffalo) helped to spread the theory and application of the rotating disk electrode to many other

electroanalytical chemists, including Dr. John Albery (Oxford University) and Dr. Denis Johnson (Iowa State University). Subsequent generations of researchers expanded on this initial work until the rotating disk electrode became a mature tool for probing electrochemical reaction kinetics.

3.11.1 The theory

The laminar flow at a rotating disk electrode conveys a steady stream of material from the bulk solution to the electrode surface. While the bulk solution far away from the electrode remains well-stirred by the convection induced by rotation, the portion of the solution nearer to the electrode surface tends to rotate with the electrode. Thus, if the solution is viewed from the frame of reference of the rotating electrode surface, then the solution appears relatively stagnant. This relatively stagnant layer is known as the hydrodynamic boundary layer, and its thickness (δ_H) can be approximated to be equal to equation 5.37

$$\delta_H = 3.6\left(\frac{v}{\omega}\right)^{1/2} \qquad 5.37$$

in terms of the kinematics viscosity of the solution (ν) and the angular rotation rate ($\omega = 2\,\pi\,f\,/\,60$), where f is the rotation rate in revolutions per minute). In an aqueous solution at a moderate rotation rate (~1000 RPM), the stagnant layer is approximately 300 to 400 μm thick. Net movement of material to the electrode surface can be described mathematically by applying general convection-diffusion concepts from fluid dynamics. Mass transport of material from the bulk solution into the stagnant layer occurs by convection (due to the stirring action of the rotating electrode). But after the material enters the stagnant layer and moves closer to the electrode surface, convection becomes less important and diffusion becomes more important. Indeed, the final movement of an ion or molecule to the electrode surface is dominated by diffusion across a very thin layer of solution immediately adjacent to the electrode known as the diffusion layer.

The diffusion layer is much thinner than the hydrodynamic layer. The diffusion layer thickness (δ_{diff}) can be approximated, according to equation 5.38:

$$\delta_{diff} = 1.61(D_F)^{1/3}v^{1/6}\omega^{-1/2} \qquad 5.38$$

in terms of the diffusion coefficient (D_F) of the molecule or ion. For a molecule or ion with a typical diffusion coefficient ($D_F \cong 10^{-5}$ cm^2/sec) in an aqueous solution, the diffusion layer is about twenty times thinner than the stagnant layer ($\delta_{diff} \cong 0.05\ \delta_H$).

The first mathematical treatment of convection and diffusion towards a rotating disk electrode was given by Levich. Considering the case where only the oxidized form of a molecule (or ion)

of interest is initially present in the electrochemical cell, the cathodic limiting current (i_{LC}) observed at a rotating disk electrode is given by the Levich equation

$$i_{L,C} = 0.620nF(D_0)^{\frac{2}{3}}\nu^{\frac{-1}{6}}C_0\omega^{\frac{1}{2}} \qquad 5.39$$

in terms of the concentration (C_O) of the oxidized form in the solution, the Faraday constant (F = 96485 coulombs per mole), the electrode area (A), the kinematic viscosity of the solution (ν), the diffusion coefficient (D_O) of the oxidized form, and the angular rotation rate (ω). On the other hand, when the solution initially contains only the reduced form, the Levich equation for the anodic limiting current (i_{LA}) can be written as

$$i_{L,A} = 0.620nF(D_R)^{\frac{2}{3}}\nu^{\frac{-1}{6}}C_R\omega^{\frac{1}{2}} \qquad 5.40$$

where the concentration term (C_R) and diffusion coefficient (D_R) are for the reduced form rather than the oxidized form.

3.11.2 Applying the Levich equation

A Levich Study is a common experiment performed using a rotating disk electrode in which a series of voltammograms is acquired over a range of different rotation rates. For a simple electrochemical system where the rate of the half reaction is governed only by mass transport to the electrode surface, the overall magnitude of the voltammogram should increase with the square root of the rotation rate (Fig. 5.14)

The currents measured during a Levich study are usually plotted against the square root of the rotation rate on a graph called a Levich plot. As predicted by the Levich equation, the limiting current (represented by the circular filled legend) increases linearly with the square root of the rotation rate (with a slope of $0.620nFDAD^{2/3}\ \nu^{-1/6}\ C$) and the line intercepts the vertical axis at zero. It is common to choose a set of rotation rates that are multiples of perfect squares (such as 100, 400, 900, 1600 RPM, etc.) to facilitate construction of this plot.

If the electrochemical half-reaction observed during a Levich study is a simple and reversible half reaction (with no complications due to sluggish kinetics or coupled chemical reactions), then the shapes of the mass-transport controlled voltammograms will be sigmoidal regardless of the rotation rate. This means that the current observed at any given potential along the voltammogram will vary linearly with the square root of the rotation rate (see plot of current versus rotation rate in Fig.16). However, it is important to remember that the Levich equation only applies to the limiting current, not to the currents along the rising portion of the sigmoid. Because the Levich equation only applies to the limiting current, the results from a Levich experiment are typically presented as a simple plot of the limiting current versus the square root of the rotation rate as shown in Fig. 5.14.

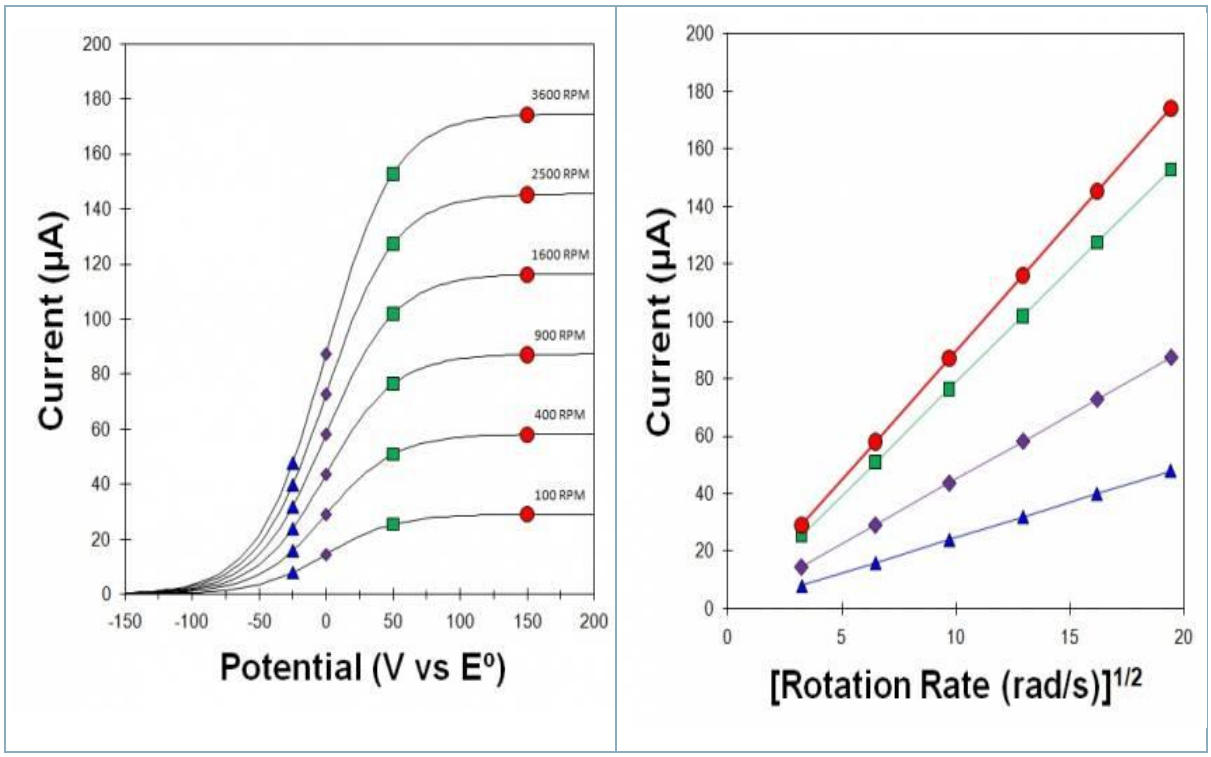


Fig. 5.14: Levich Study – Voltammograms at various rotation rates

The Levich equation can be re-arranged to the form expressed below:

$$\frac{1}{i_L} = \left(\frac{1}{0.620nFAD^{\frac{2}{3}}\nu^{\frac{-1}{6}}C}\right)\omega^{\frac{-1}{2}} \qquad 5.41$$

From equation 107, a plot of reciprocal current versus the reciprocal square root of the angular rotation rate should give a straight line called a Koutecky-Levich plot as shown in the right-hand plot in Fig. 5.15. It should be noted that for a simple and reversible half reaction with no complications the data fall along a straight line that intercepts the vertical axis at zero. If the line intercepts the vertical axis above zero, however, this is a strong indication that the half-reaction is limited by sluggish kinetics rather than by mass transport.

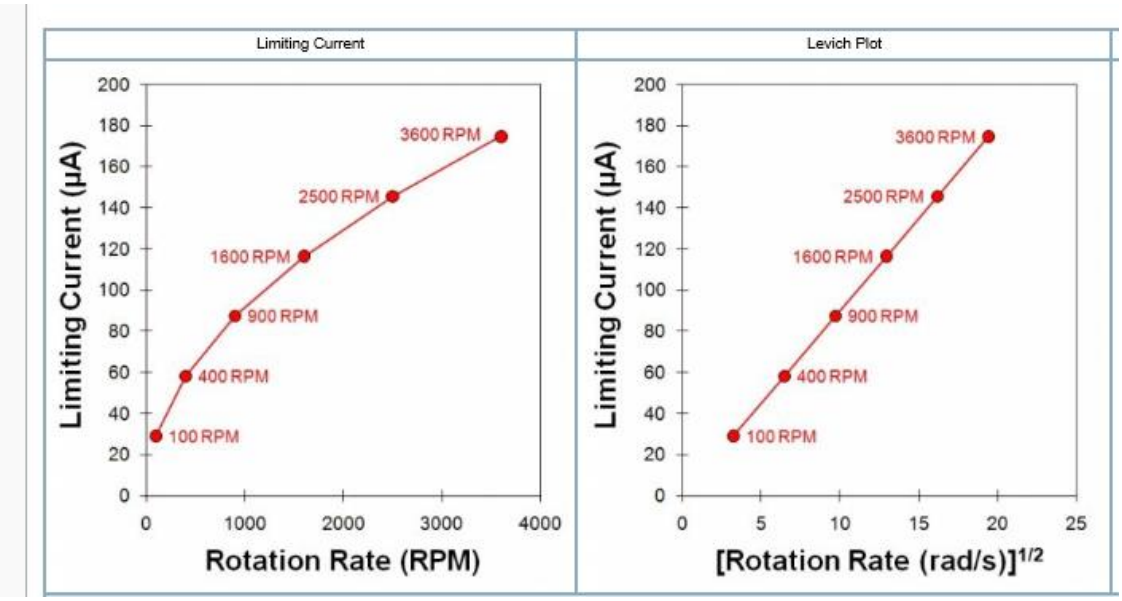


Fig. 5.15: Levich Study – Limiting Current versus Rotation Rate

4.0 (i) Self Assessment Exercises and Answers

1. 1.(a) What are the component of the Leclanche dry cell?

(b) Write the anodic and cathodic half reactions for the cell

(c) Also write the overall cell reaction for the cell

(d) The Leclanche dry cell is inexpensive to produce and is capable of producing up to 1.55 V. What are the factors that limits its efficiency?

Answer

1(a) The Leclanché dry cell is actually a "wet cell": the electrolyte is an acidic water-based paste containing MnO_2, NH_4Cl, $ZnCl_2$, graphite, and starch. The half-reactions are as follows

(b) At the cathode (reduction):

$$2MnO_{2(s)} + 2NH_4^+ + 2e^- \rightarrow Mn_2O_{3(s)} + 2NH_{3(aq)} + H_2O_{(l)}$$

At the anode (oxidation):

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^- \quad E^0_{Zn} = 0.76\,V$$

(c) The overall reaction is achieved when the zinc ion formed by the oxidation of zinc metal at the anode react with NH_3 formed at the cathode and Cl^- ions present in the solution. This gives the overall cell reaction as,

$$2MnO_{2(g)} + 2NH_4Cl_{(aq)} + Zn_{(s)} \rightarrow Mn_2O_{3(s)} + Zn(NH_3)_2Cl_2 + H_2O_{(l)}$$

(d) It is not very efficient in producing electrical energy because only the relatively small fraction of the MnO_2 that is near the cathode is actually reduced and only a small fraction of the zinc cathode is actually consumed as the cell discharges. The dry cell also has a limited

shelf life because the Zn anode reacts spontaneously with NH_4Cl in the electrolyte, causing the case to corrode and allowing the contents to leak out.

Question 2

(a) With the aid of appropriate equation, define the term, flux

(b) Define diffusion flux

(c) State the three-principal mechanism through which ions are transferred from solution to an electrode (in the absence of fluid turbulence)

(d) Write and equation to represent the rate of transfer of ion in the y-direction and relates each term in the equation to the three-principal mechanism, stated in c above

Answer

2.(a) The quantity transferred through a given area in a given amount of time is called flux. Generally, when a spatial imbalance or gradient exist for a given property, flux will occur. Generally, for a given property, flux is defined as expressed in the equation below

$$J = -k\frac{d(property)}{dx}$$

(b) The diffusion flux will be defined as the product of the diffusion coefficient and that of the diffusion gradient.

(c) In the absence of fluid turbulence, ions are transferred from solution to an electrode by three principal mechanisms:

iv. Migration: Movement of charge body under the influence of an electric field

v. Diffusion: Movement of a specie under the influence of concentration gradient

vi. Convection: This results from Stirling or hydrodynamic transport

(d) For a given species, the rate of transfer in the y-direction per unit area perpendicular to y at any point in the fluid, can be expressed according to equation

$$N_t = CU\frac{d\phi}{dx} - D\frac{\partial x}{\partial y} + VC$$

where N_t is the total rate of transfer, C is the concentration of a given specie, U is the mobility, ϕ is the potential, y is the distance in the direction of the transfer, D is the diffusion coefficient, V is the velocity of bulk

fluid movement in the direction of the transfer. The first, second and third terms of equation 61 represent the contributions from migration, diffusion and convection respectively. In the bulk only the ions are engaged in the charge transport.

Question 3

3. Write Onsager equation and compare the equation with Kohlrausch law

Answer

3. For a univalent strong electrolyte, Onsager found that, incorporating the relaxation and electrophoretic effect, leads to a relation that reveals that the molar conductivity of a univalent strong electrolyte is proportional to the square root of the concentration

$$\Lambda_c = \Lambda_0 - \left[\frac{82.4}{(DT)^{\frac{1}{2}}\eta} + \frac{8.20\times10^5}{(DT)^{\frac{3}{2}}}.\Lambda_0\right]\sqrt{C}$$

where D is the dielectric constant of the medium, T is the temperature and η is the coefficient of viscosity of the medium. The first term in the bracket (i.e. $\frac{82.4}{(DT)^{\frac{1}{2}}\eta}$) account for electrophoretic effect while the second term ($\frac{8.20\times10^5}{(DT)^{\frac{3}{2}}}$) account for relaxation effect. These terms are respective constants and can be denoted as A and B respectively. Therefore, the Onsager equation can be written as,

$$\Lambda_c = \Lambda_0 - [A + B.\Lambda_0]\sqrt{C}$$

Kohlrausch law can be written as, $\Lambda_c = \Lambda_0 - k\sqrt{C}$. Comparing this equation with Onsager equation, we have, $k\sqrt{C} = [A + B.\Lambda_0]\sqrt{C}$, indicating that $k = [A + B.\Lambda_0]$

Question 4

Derive an expression for activity coefficient of a 1:1 electrolyte

4. For a 1: 1 electrolyte consisting of a cation, A^+ and an anion, A^-. The Gibb function of these ions can be written as follows,

$$G_{A^+} = G^0_{A^+} + RTlna_{A^+} \quad 1$$

$$G_{A^-} = G^0_{A^-} + RTlna_{A^-} \quad 2$$

The average Gibb function for the two ions can be written according to equation 3

$$\frac{G_{A^+} + G_{A^-}}{2} = \frac{G^0_{A^+} + G^0_{A^-}}{2} + \frac{RT}{2}ln(a_{A^+}a_{A^-}) \quad 3$$

Also, the mean Gibb function can be written as follows,

$$\frac{G_{A^+} + G_{A^-}}{2} = \frac{G^0_{A^+} + G^0_{A^-}}{2} + RT\ln(a_{\pm}) \quad 4$$

Comparing equation 3 with 4, gives the relationship for mean activity as follows,

$$a_{\pm} = (a_{A^+}a_{A^-})^{\frac{1}{2}} \quad 5$$

Since activity is related to the activity coefficient, i.e. $a = \gamma C$, we can also develop similar equation in terms of γ as follows,

$$\gamma_{\pm} = ([C_{A^+}\gamma_{A^+}][C_{A^-}\gamma_{A^-}])^{\frac{1}{2}} = (C_{A^+}C_{A^-})^{\frac{1}{2}}.(\gamma_{A^+}\gamma_{A^-})^{\frac{1}{2}}$$

However, activity coefficient takes care of concentration hence the above equation can be written as equation 6,

$$\gamma_{\pm} = (\gamma_{A^+}\gamma_{A^-})^{\frac{1}{2}} \quad 6$$

Generally for a salt represented as A_xB_y,, which dissolves to give a solution of x cation and y anion, the mean activity coefficient can be written according to equation 7

$$\gamma_{\pm} = (\gamma_+^x \gamma_-^y)^{\frac{1}{s}} \quad 7$$

where s = x + y.

5. Zinc chloride ionizes as follows,

$$ZnCl_{2(s)} \rightarrow Zn^{2+}_{(aq)} + 2Cl^-_{(aq)}$$

From the equation, 0.04 M of $ZnCl_2$ ionizes to give 0.08 M of Cl^- and 0.04 M Zn^{2+}. The mean ionic molarity can be written as, $m_{\pm} = (m_+^{v+}m_-^{v-})^{\frac{1}{v+ +V-}}$, which can be simplified to suite the present case, thus $m_{\pm} = \left(m_{Zn}^{Zn(v+)}m_{Cl}^{Cl(v-)}\right)^{\frac{1}{Zn(v+)+Cl(v-)}}$. Therefore,

$$m_{\pm} = \left(m_{Zn}^{Zn(v+)}m_{Cl}^{Cl(v-)}\right)^{\frac{1}{Zn(v+)+Cl(v-)}} = ((0.04)^1.(0.08)^2)^{\frac{1}{1+2}} = (0.000256)^{\frac{1}{3}}$$
$$= 6.3514 \times 10^{-2}$$

The mean ionic activity coefficient can be calculated using the equation, $log\gamma_{\pm} = -A|z_+z_-|I^{\frac{1}{2}}$ where I is the ionic strength which is given as, $I = \frac{1}{2}\sum_i z_i^2 C_i$. The ionic strength of $ZnCl_2$ can therefore be calculated thus,

$$I = \frac{1}{2}\sum_i z_i^2 C_i = \frac{1}{2}\sum_i (0.04)(+2)^2 + (0.08)(-1)^2 = 0.12$$

Mean activity coefficient $log\gamma_{\pm} = -A|z_+z_-|I^{\frac{1}{2}} = log\gamma_{\pm} = -0.509|(2)(1)|(0.12)^{\frac{1}{2}}$
$$= -0.3526$$

That is $log\gamma_{\pm} = -0.3526$, hence, $\gamma_{\pm} = log^{-1}(-0.3526) = 2.2528$

Question 6

(a)Conductivity of an electrolyte is proportional to some parameters. List the parameters and define the term, mobility

(b) Given that $F = eEz = \frac{ze\Delta\phi}{L}$. Derive an expression for the transport number of cation and anion

Answer

6.(a) It has been found that the conductivity of a electrolyte is proportional to the following parameters,

iv. The mobility of the ion

v. The concentration of the ion

vi. Charge of the ion.

Mobility is defined as the limiting velocity of ion in an electric field of unit strength. Therefore, if the strength of an electric field is E, then the force exerted is given by

$$F = eEz = \frac{ze\Delta\phi}{L}$$

(b) $$F = eEz = \frac{ze\Delta\phi}{L} \qquad 1$$

where e is the electronic charge, z is the charge of the ion and $\Delta\phi$ is the potential difference between two electrodes separated by a distance, L. However, in electrochemical system, ions in motions experience an opposing frictional force, which can be expressed according to Stokes law:

$$F_{fric} = 6\pi\eta rv \qquad 2$$

whereη is the viscosity of the electrolyte, r is the radius of the ion and v is the velocity of the ion in solution (i.e. driftspeed). A system of this type attains a terminal velocity when the accelerating and the retarding forces counterbalance each other. Therefore,

$$6\pi\eta rv = eEz$$

$$v = \frac{eEz}{6\pi\eta r}$$

This terminal velocity is termed the mobility (u) defined as $u = \frac{v}{E}$. Therefore

$$u = \frac{ze}{6\pi\eta} \qquad 3$$

The molar conductivity of an electrolyte is defined as, $\lambda = zuF$and for cation and anion, the molar conductivities are given by equation 4 and 5 respectively,

$$\lambda_+ = z_+Fu_+ \qquad 4$$

$$\lambda_- = z_-Fu_- \qquad 5$$

where F is the Faraday's constant. On the other hand, the specific conductivity or conductance of an electrolyte is defined according to equation 6

$$k = Fzuvc \qquad 6$$

where v is the number of cation or anion per formula unit of the electrolyte. Transport number of cation or anion can then be expressed as the ratio of the contribution made by the cation or anion to the total current carried in solution. Thus,

$$t_+ = \frac{z_+u_+C_+}{\Sigma z_iC_iu_i} \qquad 7$$

$$t_- = \frac{z_-u_-C_-}{\Sigma z_iC_iu_i} \qquad 8$$

(ii) Class Activity

(1) Explain the principles behind the following cells (1) Fuel cell (ii) Hydrogen cell (ii) Alkaline cell (20 minutes)

5.0 Conclusion

Mass transport is essential process in electrochemical systems. Materials can be transported by migration (basically charge), diffusion and convection. It is significant to note that mass transport by migration and diffusion dominate most electrochemical systems compared to convection. In order to encourage mass transport by convection, some external forces (such as thermal agitation) must be introduced into the system. Relevant laws in the field of mass transport is Fick's first and second law. The Levich law is another law that explain some mechanism of mass transfer. Although the Levich law is derived based on a rotating disc electroscope, it is significant in analytical electrochemistry.

6.0 Summary

The Levich Equation models the diffusion and solution flow conditions around an RDE (RDE). It is named after Veniamin Levich who first developed an RDE as a tool for electrochemical research. It can be used to predict the current observed at an RDE, in particular, the Levich equation gives the height of the sigmoidal wave observed in rotating disk voltammetry. The sigmoidal wave height is often called the Levich current.

The Levich equation can be written as: $i_{L,C} = 0.620nF(D)^{\frac{2}{3}}v^{\frac{-1}{6}}C\omega^{\frac{1}{2}}$

where I_L is the Levich current (A), *n* is the number of electron transferred in the half reaction (mol^{-1}), F is the Faraday constant (C/mol), A is the electrode area (cm^2), *D* is the diffusion coefficient (cm^2/s), *w* is the angular rotation rate of the electrode (rad/s), *v* is the kinematic viscosity (cm^2/s) and C is the analyte concentration (mol/cm^3)

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Link to slide show:https://www.slideshare.net/GamryInstruments/echem-basics-for-users

MODULE 3

STUDY UNIT 2:POLAROGRAPHY

1.0 Introduction

2.0 Learning Outcome

3.0 Main Content

3.1 Theory and principles of polarography

3.1.1 Diffusion current

3.1.2 The half wave potential and its significance

4.0 (i) Self Assessment Exercises and Answer

(ii) Class Activity

5.0 Conclusion

6.0 Summary

7.0 References/Further Readings

1.0 Introduction

The first scientist who discovered the use of the DME in electrolysis is Jaroslave Heyrovsky in 1922 and received the Nobel Prize in Chemistry in 1959. Polarography was the first of the voltammetric techniques to gain prominence. The most popular constant potential method is d.c. polarography at a dropping mercury electrode (DME).

Polarography is the branch of voltammetry in which a dropping mercury electrode is used as the indicator electrode. It is the electroanalytical technique that deals with the effect of the potential of an electrode in an electrolysis cell on the current that flows through it. The electrode whose potential is varied is called the indicator electrode voltammetric indicator electrodes may be made from quite a large number of materials such mercury, platinum, gold and graphite, having varying shapes and construction. They may be stationary or is motion and the solutions in which these are used may be stationary or quiet.

2.0 Intended Learning Outcomes

When you have studied this session, you should be able to:

i. understand what is polarography
ii. know the principles of polarography
iii. Know what are the physical problems that can be handled using polarography
iv. derive the Ilkovic equation and explain the significant of basic terms in the equation
v. sketch a plot for a typical pattern of a polarogram
vi. solve some problems related to polarography

3.0 Main Content

3.1 Theory and principles of polarography

The first scientist who discovered the use of the DME in electrolysis is Jaroslave Heyrovsky in 1922 and received the Nobel Prize in Chemistry in 1959. Polarography was the first of the voltammetric techniques to gain prominence. The most popular constant potential method is d.c. polarography at a dropping mercury electrode (DME).

Polarography is the branch of voltammetry in which a dropping mercury electrode is used as the indicator electrode. It is the electroanalytical technique that deals with the effect of the potential of an electrode in an electrolysis cell on the current that flows through it. The electrode whose potential is varied is called the indicator electrode voltammetric indicator electrodes may be made from quite a large number of materials say for instance mercury, platinum, gold and graphite, having varying shapes and construction. They may be stationary or is motion and the solutions in which these are used may be stationary or quiet.

Polarography is the study of the electrolysis of solutions of electro-oxidizable and or electro-reducible substances between a dropping mercury electrode (DME) and some reference electrode (RE). The potential between these electrodes is varied and the consequent changes in the flow of current is measured. On plotting the changes in current flow versus the potential variation, one obtains ani-E curve known as polarogram (Fig.6.1).

The slowly increasing current at the foot of the wave is known as the residual current. This current is non faradaic in nature. The diffusion current i_d is, as shown, the distance between the limiting diffusion plateau and the residual current. The potential at the midpoint of the wave, where the current is exactly half its limiting value, is known as the half-wave potential $E^{1/2}$ and its quantity is characteristic of a particular species under fixed experimental conditions. Thus $E^{1/2}$ value serves as finger-print for the species undergoing redox reaction.

In addition, the limiting current is proportional to concentration of the species being reduced or oxidized and thus serves for quantitative analyses. Over the diffusion current plateau region, the DME is behaving as a completely polarized electrode since it adopts any applied potential to it with no change in current flow. It is significant to note that polarization always results from slow stage in the overall electrode process. The slow stage here is the diffusion process which occurs very much slower than the electron transfer. This type of polarization is known as concentration polarization and the DME is said to be concentration polarized. At potentials corresponding to the rising part of the wave the electrode is depolarized since here the current

flow is strongly dependent on the applied potential. At this stage it is important to emphasize that in any electrolysis two types of processes are encountered.

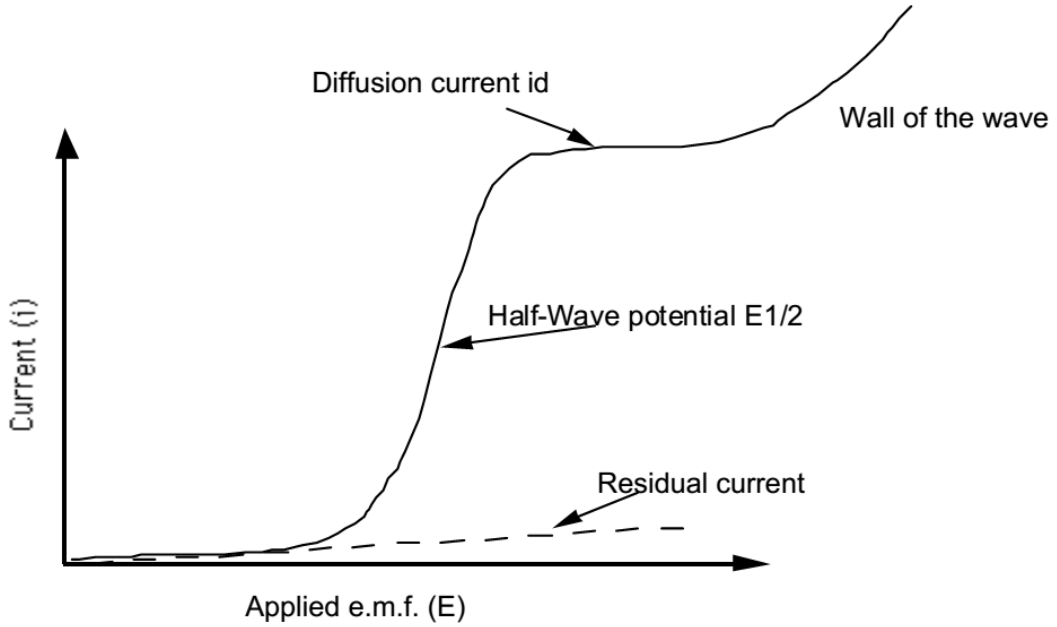


Fig. 6.1: Typical pattern of a polarogram

i. Mass transfer process which brings the electroactive material to the electrode surface

ii. Electrochemical process which involves the act of electron transfer between the surface of electrode and the electroactive species.

As stated before, mass transfer is usually achieved through migration, diffusion and convection. Migration is an electric field effect and depends upon the charge on the species, concentration and mobility in a field of force. Diffusion depends upon differences in concentration between species at the surface of the electrode and in the bulk of solution. Finally, convection arises from any mechanical or thermal disturbance in the solution. For a redox process to occur it is essential that electrons pass between the electrode and the species in solution. However, before electron transfer can be effective, processes such as adsorption and rearrangement of electronic configuration within the species must occur in order to give a suitable form for the electron exchange. After the electron exchange, a primary product is formed which re-undergoes an electronic rearrangement, desorption and may suffer further side reactions to form the final product. These electrolytic processes may be reversible or irreversible in nature depending on the activation energy values.

3.1.1 Diffusion Current, i_d

According to Fick's first law of diffusion, the rate of diffusion is proportional to the concentration gradient. Since diffusion in polarography is the rate determining step, the rate of diffusion can be equated to the rate of electrode reaction. Hence the rate of the electrode reaction is proportional to the concentration gradient. That is,

$$Rate of diffusion \alpha \left(\frac{dC}{dx}\right)(x = 0) \qquad 6.1$$

Equation 6.1 can also be written as follows,

$$\frac{i}{nFA} \alpha \left(\frac{dC}{dx}\right)(x = 0) \qquad 6.2$$

Simplification of equation 6.2 yields equation 6.3

$$i = nFAD \left(\frac{dC}{dx}\right)(x = 0) \qquad 6.3$$

where A is the surface area of a plane electrode, across which a current i passes due to the impressed emf, n is the number of electrons, F is the Faraday, D is the diffusion coefficient in cm^2/sec., C is the concentration, x = 0 means at the electrode surface.

As stated before, under polarization, if the concentration of the active specie on the surface and bulk are C_S and C_B, then the concentration gradient is, $\frac{dC}{dx} = \frac{(C_B - C_S)}{\delta}$ and by substitution into equation 6.3, equation 6.4a is obtained,

$$i = nFAD \left(\frac{C_B - C_S}{\delta}\right) \qquad 6.4a$$

Also, as stated earlier, maximum current will flow in the cell when C_S =0 and the current that flows under this condition is called limiting current (i_L), which is equal to diffusion current in this case, hence,

$$i_d = nFAD \left(\frac{C_B}{\delta}\right) \qquad 6.4b$$

where i_d is the maximum limiting current. Fick's first law is limited only for the cases where the diffusion layer is of constant thickness and where the conditions are stationary. In other cases when the diffusion layer thickness alters with time and concentration is varying with both time and distance, Fick's second law is most appropriate written as equation 6.5

$$\frac{dC}{dt} = D \left(\frac{d^2C}{dx^2}\right) \qquad 6.5$$

Fick's second law (equation 6.5) can only be solved mathematically by Laplace integral transform resulting in the Cottrell equation. This equation reveals that i_t decreases with time due to a broadening of the diffusion layer and a decrease in the diffusion rate. Equation 6.5 is the backbone of the Ilkovic equation. Generally, i_t can be written as follows,

$$i_t = nFAD^{\frac{1}{2}} C_B \pi^{\frac{1}{2}} t^{\frac{1}{2}} \qquad 6.6$$

In order to convert equation 6.6 into Ilkovic equation, we assumes that the drop is spherical and that the mercury flow rate is uniform, that is , that the drop volume increases linearly with time. Which implies that it's $A = 4\pi r^2$, $V = (4/3)\pi r^3$, $d = W/V$ and $V = W/V = 10^{-3}mt/d$. Combining these functions, we have the values for the radius (equation 6.7):

$$r = \left(\frac{[3 \times 10^{-3} mt]}{[4d]}\right)^{\frac{1}{3}} \qquad 6.7$$

If we replace value of r into the formula for calculating area (i.e. $A = 4\pi r^2$), then:

$$A = \left(\frac{6 \times 10^{-3} \pi^{\frac{1}{2}} mt}{d}\right)^{\frac{2}{3}} \qquad 6.8$$

Substituting for A in equation 6.5 (using equation 6.8), we obtained equation 6.9, which simplifies to equation 6.10

$$i_t = \left\{\left(nFC_B D^{\frac{1}{2}} t^{\frac{1}{6}}\right)/\pi^{\frac{1}{6}}\right\}\{(6 \times 10^{-3} m)/d\}^{\frac{2}{3}}\left(\frac{7}{3}\right)^{1/2} \qquad 6.9$$

$$i_d = 708nD^{\frac{1}{2}} t^{\frac{1}{6}} m^{\frac{2}{3}} C_B \qquad 6.10$$

where V is the volume in cm^3, W is the weight of the drop in g, m is the rate of Hg flow in mg/sec, d is the density g/cm^3, (7/3) 2/3 is introduced to account for the fact that the drop is continually expanding. Equation 6.10 is called the Ilkovic equation where i_d is expressed in μA, C_B in mM per liter and t in seconds. The equation is a linear equation of the form, $i_d = KC_B$. This linear relation is the basis of quantitative analyses (calibration curve) in polarography

3.1.2 The half-wave potential and its significance

The most important constant in polarography is the half-wave potential. Chemical, thermodynamic and structural information may be obtained from the measurements of the half-wave potentials of reversible and irreversible waves under varying experimental conditions.

The manner in which the current is affected by electrode potential on the rising part of the wave is to be noted. On the plateau, electron transfer is so fast that the ions or molecules of the electroactive substances are reduced or oxidized as rapidly as they arrive or are formed at the electrode surface. As the potential moves from the plateau of the wave towards its foot, the rate of the electron-transfer process decreases and the reduction or oxidation becomes less and less complete. It is convenient to divide electrode reactions into two extreme classes:

(i) Reversible reactions, and

(ii) irreversible reactions.

The reversible reactions are so rapid that thermodynamic equilibrium is very nearly attained at every instant during the life of a drop at any potential. For such reactions the variation of current

with potential reflects the changing position of the equilibrium and is described by Nernst equation. The other extreme is that of totally irreversible reactions, which are so slow that they proceed only by a fraction of the way towards equilibrium during the life of each drop. For these reactions it is the rate of the electron-transfer process and the manner in which this is influenced by the electrode potential that governs the relationship between current and potential. The polarographic data serve to elucidate the kinetics of the rate determining step in totally irreversible processes.

Worked example 1

(a) What is polarography and polarogram

(b) Draw a typical diagram to show polarogram and indicate the position of diffusion current, wall of the wave, half wave potential and residual current on the diagram

(c) Define the following terms with respect to polarography

i. Residual current

ii. Half wave potential

iii. Diffusion current

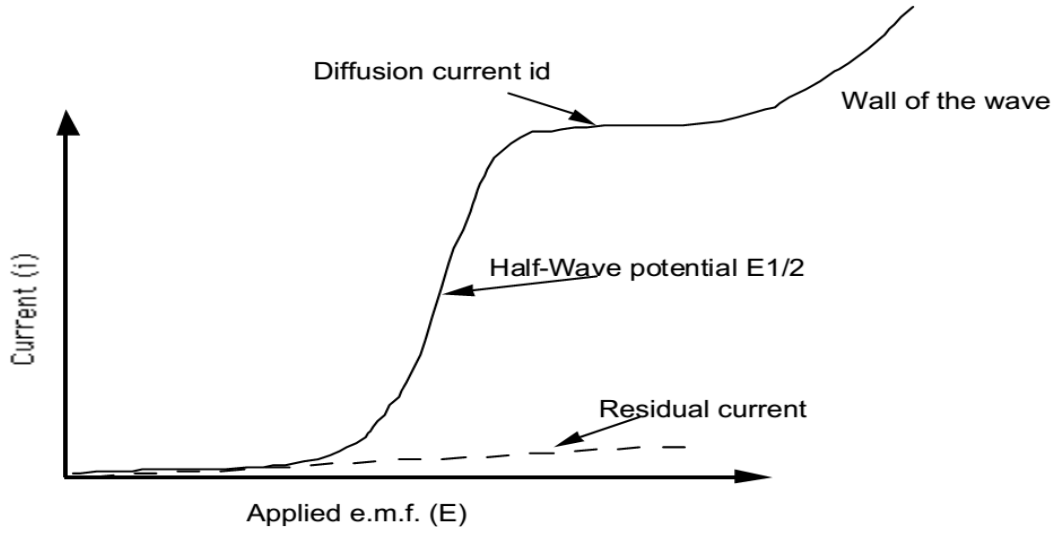
\(c) Given the following values for a dropping mercury electrode, calculate the diffusion current using the Ilkovic equation n = 2, D = 4.0, t = 64s, m = 8 and C = 2.3 M (all in S.I unit)

Solution

(a) Polarography is the study of the electrolysis of solutions of electro-oxidizable and or electro-reducible substances between a dropping mercury electrode (DME) and some reference electrode (RE). The potential between these electrodes is varied and the consequent changes in the flow of current is measured.

A plot representing changes in current flow against the applied potential is called a polarogram.

(b)



Typical pattern of a polarogram

(i) The slowly increasing non-Faradic current at the foot of the wave is known as the residual current.

(ii) The potential at the midpoint of the wave, where the current is exactly half its limiting value, is known as the half-wave potential $E^{1/2}$

(iii) The diffusion current i_d is, as shown, the distance between the limiting diffusion plateau and the residual current.

3.1.3 Factors affecting the half-wave Potentials

1. The temperature coefficient of the half-wave potential is mostly between –2 and +2 mv/degree. For a reversible wave it may be either positive or negative. For an irreversible wave it is usually positive and may exceed several millivolts per degree.

2. The half wave potential is almost always independent of the concentration of the electroactive species (i.e., of the diffusion current) after proper correction is applied for the iR drop. However, the half-wave potential of a reversible wave does not vary with concentration if a solid product is termed, or more generally, whenever the number of the ions or molecules of the product of variable activity differ from the number of ions or molecules of reactant of variable activity in the equation for the half-reaction. Such variations can be described only by thermodynamic equations. The half-wave potential of an irreversible wave may also vary with concentration of the reaction mechanism involving some rate governing step that is not the first- or pseudo-first order. When it does vary, it most often becomes more negative as the concentration increases.

3. The half-wave potential of a reversible wave is nearly independent of the capillary characteristics, i.e., mass (m) and time (t). When the diffusion current obeys the Koutocky equation and when the diffusion coefficient of the oxidized and reduced species differs a small dependence of the half-wave potential on $t^{1/6}$ and $m^{1/3}$ can be predicted. Changes in m, t and the concentration of the electroactive species can produce apparent variations of the half-wave potential unless both are corrected. The iR drop always produces an apparent shift of the half-wave potential toward more negative values for the cathodic waves and toward more positive values for anodic waves and the shift is proportional to the limiting current.

4. Changes in the nature and concentration of supporting electrolyte may affect the half-wave potential in many ways. For reversible waves the effect is due to complex formation.

5. When a complex metal ion is reversibly reduced to a metal soluble in mercury, its half-wave potential is always more negative than that for the reversible reduction of the corresponding simple or aquo-complex ion. Complex formation may cause the half-wave potential in the irreversible reduction of a metal ion to become either more negative or more positive. This depends on the nature of the ligand used.

Worked example 2

Given the following values for a dropping mercury electrode, calculate the diffusion current using the Ilkovic equation n = 2, D = 4.0, t = 64s, m = 8 and C = 2.3 M (all in S.I unit)

Solution

The Ilkovic equation can be written as,

$$i_d = 708nD^{\frac{1}{2}}t^{\frac{1}{6}}m^{\frac{2}{3}}C_B$$

$$i_d = 708(2)(4)^{\frac{1}{2}}(64)^{\frac{1}{6}}(8)^{\frac{2}{3}}(2.3)$$

$$= 708 \times 2 \times 2 \times 2 \times 4 \times 2.3 = 52108.8\ A$$

4.0 (i) Self Assessment Exercise and Answers

1.(a) What is polarography?

(b) Write short note on voltametric indicator electrode

(c) Sketch a polarogram. On your sketch, labelled and explain the following, residual current, diffusion current, half wave potential

2.(a) Identify the two major processes that takes place in an electrolytic cell

(b) What are the factors that enhance mass transfer in an electrolytic cell? Hence what are the parameters the stated factors depend on

(c) What is the essential requirement for a redox reaction to occur in polarography cell?

(d) What are the relevant processes that are required before electron transfer can effective?

(e) Highlight processes that occurs after electron exchange in polarography cell

3. (a) State Fick's law of diffusion that is relevant for polarography

(b) Use the stated Fick's law to derived the expression, $i_t = nFAD^{\frac{1}{2}}C_B\pi^{\frac{1}{2}}t^{\frac{1}{2}}$

(c) Use the expression derived from Fick's law to derive Ilkovic equation

4.(a) What are the two extreme ways that electrode reactions can be conveniently grouped into?

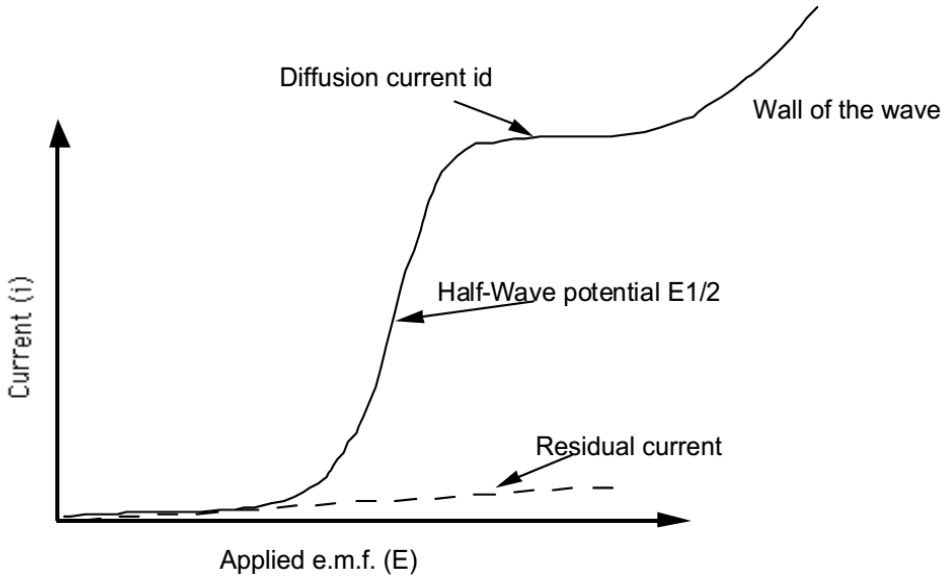
(b) Write short note on reversible and irreversible electrode reaction

Answers to Self Assessment Exercises

1.(a) Polarography is the branch of voltammetry in which a dropping mercury electrode is used as the indicator electrode. It is the electroanalytical technique that deals with the effect of the potential of an electrode in an electrolysis cell on the current that flows through it.

(b) The electrode whose potential is varied is called the indicator electrode voltammetry indicator electrodes may be made from quite a large number of materials such mercury, platinum, gold and graphite, having varying shapes and construction. They may be stationary or is motion and the solutions in which these are used may be stationary or quiet.

(c) As shown in the sketch below, the slowly increasing current at the foot of the wave is known as the residual current. This current is non faradaic in nature. The diffusion current i_d is, as shown, the distance between the limiting diffusion plateau and the residual current. The potential at the midpoint of the wave, where the current is exactly half its limiting value, is known as the half-wave potential $E^{1/2}$ and its quantity is characteristic of a particular species under fixed experimental conditions. Thus $E^{1/2}$ value serves as finger-print for the species undergoing redox reaction.



2(a) The two major processes in electrolytic cell are

iii. Mass transfer process which brings the electroactive material to the electrode surface

iv. Electrochemical process which involves the act of electron transfer between the surface of electrode and the electroactive species.

(b) Mass transfer is usually achieved through migration, diffusion and convection. Migration is an electric field effect and depends upon the charge on the species, concentration and mobility in a field of force. Diffusion depends upon differences in concentration between species at the surface of the electrode and in the bulk of solution. Finally, convection arises from any mechanical or thermal disturbance in the solution.

(c) For a redox process to occur it is essential that electrons pass between the electrode and the species in solution.

(d) Before electron transfer can be effective, processes such as adsorption and rearrangement of electronic configuration within the species must occur in order to give a suitable form for the electron exchange.

(e) After the electron exchange, a primary product is formed which re-undergoes an electronic rearrangement, desorption and may suffer further side reactions to form the final product. These electrolytic processes may be reversible or irreversible in nature depending on the activation energy values.

3. (a) According to Fick's first law of diffusion, the rate of diffusion is proportional to the concentration gradient.

(b) Since diffusion in polarography is the rate determining step, the rate of diffusion can be equated to the rate of electrode reaction. Hence the rate of the electrode reaction is proportional to the concentration gradient. That is,

$$Rate of diffusion \alpha \left(\frac{dC}{dx}\right)(x = 0) \qquad 1$$

Equation 20 can also be written as follows,

$$\frac{i}{nFA} \alpha \left(\frac{dC}{dx}\right)(x = 0) \qquad 2$$

Simplification of equation 2 yields equation 3

$$i = nFAD \left(\frac{dC}{dx}\right)(x = 0) \qquad 3$$

where A is the surface area of a plane electrode, across which a current i passes due to the impressed emf, n is the number of electrons, F is the Faraday, D is the diffusion coefficient in cm^2/sec., C is the concentration, x = 0 means at the electrode surface.

As stated before, under polarization, if the concentration of the active specie on the surface and bulk are C_S and C_B, then the concentration gradient is, $\frac{dC}{dx} = \frac{(C_B - C_S)}{\delta}$ and by substitution into equation 3, equation 4 is obtained,

$$i = nFAD \left(\frac{C_B - C_S}{\delta}\right) \qquad 4$$

Also, as stated earlier, maximum current will flow in the cell when C_S =0 and the current that flows under this condition is called limiting current (i_L), which is equal to diffusion current in this case, hence,

$$i_d = nFAD \left(\frac{C_B}{\delta}\right) \qquad 5$$

where i_d is the maximum limiting current. Fick's first law is limited only for the cases where the diffusion layer is of constant thickness and where the conditions are stationary. In other cases when the diffusion layer thickness alters with time and concentration is varying with both time and distance, Fick's second law is most appropriate written as equation 6

$$\frac{dC}{dt} = D \left(\frac{d^2C}{dx^2}\right) \qquad 6$$

Fick's second law (equation 6.5) can only be solved mathematically by Laplace integral transform resulting in the Cottrell equation. This equation reveals that i_t decreases with time due to a broadening of the diffusion layer and a decrease in the diffusion rate. Equation 6 is the backbone of the Ilkovic equation. Generally, i_t can be written as follows,

$$i_t = nFAD^{\frac{1}{2}} C_B \pi^{\frac{1}{2}} t^{\frac{1}{2}} \qquad 7$$

(c) In order to convert equation 6.6 into Ilkovic equation, we assume that the drop is spherical and that the mercury flow rate is uniform, that is, that the drop volume increases

linearly with time. Which implies that it's $A = 4\pi r^2$, $V = (4/3)\pi r^3$, $d = W/V$ and $V = W/V = 10^{-3}mt/d$. Combining these functions, we have the values for the radius (equation 8a):

$$r = \left(\frac{[3 \times 10^{-3} mt]}{[4d]}\right)^{\frac{1}{3}} \qquad 8a$$

If we replace value of r into the formula for calculating area (i.e. $A = 4\pi r^2$), then:

$$A = \left(\frac{6 \times 10^{-3} \pi^{\frac{1}{2}} mt}{d}\right)^{\frac{2}{3}} \qquad 8b$$

Substituting for A in equation 8b (using equation 7), we obtained equation 9, which simplifies to equation 10

$$i_t = \left\{\left(nFC_B D^{\frac{1}{2}} t^{\frac{1}{6}}\right)/\pi^{\frac{1}{6}}\right\}\{(6 \times 10^{-3} m)/d\}^{\frac{2}{3}}\left(\frac{7}{3}\right)^{1/2} \qquad 9$$

$$i_d = 708 n D^{\frac{1}{2}} t^{\frac{1}{6}} m^{\frac{2}{3}} C_B \qquad 10$$

where V is the volume in cm^3, W is the weight of the drop in g, m is the rate of Hg flow in mg/sec, d is the density g/cm^3, (7/3) 2/3 is introduced to account for the fact that the drop is continually expanding. Equation 10 is called the Ilkovic equation where i_d is expressed in μA, C_B in mM per liter and t in seconds. The equation is a linear equation of the form, $i_d = KC_B$. This linear relation is the basis of quantitative analyses (calibration curve) in polarography

a) It is convenient to divide electrode reactions into two extreme classes:

(iii) Reversible reactions, and

(iv) irreversible reactions.

(b) **The reversible reactions** are so rapid that thermodynamic equilibrium is very nearly attained at every instant during the life of a drop at any potential. For such reactions the variation of current with potential reflects the changing position of the equilibrium and is described by Nernst equation.

The other extreme is that of totally irreversible reactions, which are so slow that they proceed only by a fraction of the way towards equilibrium during the life of each drop. For these reactions it is the rate of the electron-transfer process and the manner in which this is influenced by the electrode potential that governs the relationship between current and potential. The polarographic data serve to elucidate the kinetics of the rate determining step in totally irreversible processes.

(ii) Class Activity

(1) Sketch a typical polarogram and explain all the information and parameters that can be deduced from such plot (20 minutes)

5.0 Conclusion

Polarography is a subclass of voltammetry where the working electrode is a dropping mercury electrode (DME) or a static mercury drop electrode (SMDE), which are useful for their wide cathodic ranges and renewable surfaces.

6.0 Summary

Polarography is a voltammetric measurement whose response is determined by combined diffusion/convection mass transport. Simple principle of polarography is the study of solutions or of electrode processes by means of electrolysis with two electrodes, one polarizable and one unpolarizable, the former formed by mercury regularly dropping from a capillary tube. Polarography is a specific type of measurement that falls into the general category of linear-sweep voltammetry where the electrode potential is altered in a linear fashion from the initial potential to the final potential. As a linear sweep method controlled by convection/diffusion mass transport, the current vs. potential response of a polarographic experiment has the typical sigmoidal shape. Polarography is based on the principle of mass transport and it is a method that has been widely used in laboratory and industrial analysis Although it has some limitation, it has found wider application in analysing for the underlisted parameters in pharmaceutical products

- Dissolved oxygen and peroxides.
- Trace metals and metal-containing drugs.
- Antiseptics and insecticides.
- Vitamins.
- Hormones.
- Antibiotics.
- Alkaloids.
- Blood serum and cancer diagnosis.

Therefore, the study of polarography is sustained by its wider applications in industries.

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MODULE 3

STUDY UNIT 3: ELECTRONICS IN ELECTROCHEMISTRY

1.0 Introduction

2.0 Intended Learning Outcomes

3.0 Main Content

3.1 Electronics and instrumentation

3.2 Transducer and detector

3.3 Electrochemical circuit

3.4 Polarization circuit

3.5 Circuits for emf measurements

3.6 Electrochemical impedance spectroscopy

4.0 (i) Self Assessment Exercises and Answers

(ii) Class Activity

5.0 Conclusion

6.0 Summary

7.0 References/Further Readings

1.0 Introduction

Electronics is the science of how to control the electrical energy, in which the electrons have a fundamental role. Electronics deals with electrical circuits that involve active electrical components such as vacuum tubes, transistors, diodes and integrated circuits, and associated passive electrical components and interconnection technologies. Commonly, electronic devices contain circuitry consisting primarily or exclusively of active semiconductors supplemented with passive elements; such a circuit is described as an electronic circuit. Most electrochemical instruments rely on the measuring of some physical process for example amount of current, voltage, resistant, capacitance, etc. Generally, an electrochemical instrument will have a signal as the input, a transducer, signal processor and read out system as the functional element (Fig. 7.1)

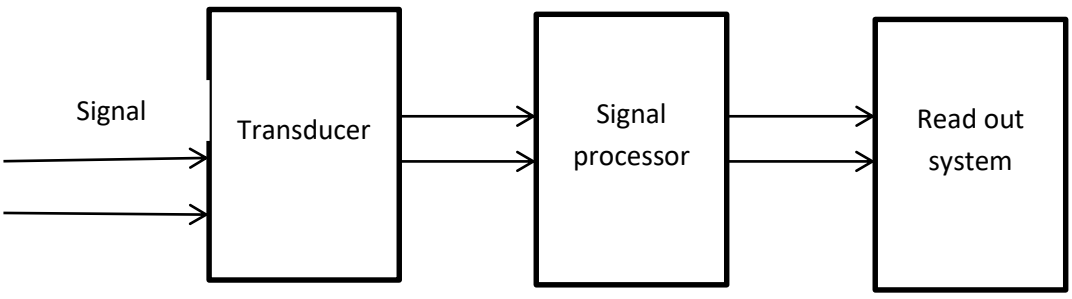


Fig. 7.1: Block diagram of a measuring instrument

Input signal enters the instrument through the transducer. The transducer produces an internal signal which has to be amplified before it can be read from the read-out system. A signal represents some form of information or a means of carrying the information. A transducer is a functional element of an instrument which receives the input signal and produces an output signal (internal signal) that has to pass through a signal processor. All transducers work through some form of physical properties.

2.0 Intended Learning Outcome

When you have studied this session, you should be able to:

i. know the basic elements needed in electrochemical instruments
ii. understand the importance of circuits in electrochemistry
iii. understand the functions of transducer and detector in electrochemical instruments
iv. examine some electrochemical cells and the mechanism of flow of electrons within the cell

3.0 Main Content

3.1 Electronics and instrumentation in electrochemistry

3.1.1 Transducer and detector

A transducer is used to convert energy or information (input signal) from one form to another. The pH electrode for example is a transducer that responds to a change in the potential difference between a liquid in a sealed glass and the sample solution to be measured. A pH electrode consists of a glass bulb that contains 0.1 MHCl saturated with AgCl. However, for analytical purpose, the pH meter has to be used in conjunction with a reference electrode. The common type of a reference electrode is the colomel electrode. The pH electrode is sensitive to pH change. It is a thin membrane of special glass, which separates the solution being tested from a saturated solution of AgCl. Most pH meters 'electrodes combine the features of the pH electrode and that of the reference electrode into a single electrode called combination electrode.

When the glass electrode is inserted into a solution for analytical purpose, a voltage difference is generated between the two surfaces of the glass membrane and the magnitude of the generated voltage depends on the pH of the solution being tested. Theoretical voltage output from a pH meter can be calculated from the Nernst equation. The chemical equation that is significant in pH study is expressed in equation 7.1

$$H^+ + e^- = \tfrac{1}{2} H_2 \qquad 7.1$$

Applying the Nernst equation to equation 7.1, we have equations 7.2 and 7.3:

$$E_H = E^0 - \frac{2.303RT}{F} log a_{H^+}^{+} \quad 7.2$$

$$E_H = E^0 - \frac{2.303RT}{F} pH \quad 7.3$$

Equation 7.3 can be simplified to equation 7.4

$$E_v - E_0 = -0.198T(pH - 7.0) \quad 7.4$$

where E_V is the voltage being measured in millivolt and T is the temperature of the solution in Kelvin. The value of E_0 depends on the particular electrode being used and is almost constant for a given electrode.

Other types of electrode that operates in similar principles are ion selective electrodes (electrochemical transducers) which are sensitive to a particular ion. Generally, in all electrochemical instruments, the output signal determined the type of signal processor that is required. The sensitivity of a transducer is defined as the ratio of the magnitude of the output signal to the magnitude of the input signal. Its selectivity is also defined as the ratio of its sensitivity to the input signal (to be measured) to the sensitivity to other input signal.

3.2 Electrochemical circuits

Electrochemistry can be defined as the branch of chemistry that deals with chemical reactions which take place at the interface of an electrode, usually a solid metal or a semiconductor, and an ionic conductor, the electrolyte. These reactions therefore involve the movement of electric charges between the electrodes and the electrolyte (or ionic species in a solution). Hence, electrochemistry deals with the interaction between electrical energy and chemical change.

A chemical reaction caused by an externally supplied current, such as electrolysis, or if an electrical current is produced by a spontaneous chemical reaction as in a battery, it is called an electrochemical reaction. Chemical reactions where electrons are transferred directly between molecules and ions are called oxidation-reduction or (redox) reactions. In general, electrochemistry describes the overall reactions when individual redox reactions are separate but connected by an external electric circuit and an intervening electrolyte.

From the above, it can be seen that electrochemical reactions involves the interaction of charged ions or electrons. They must be a power source, electrolyte and electrodes. Other circuit elements such as galvanometer, voltammeter and others, may be useful. Hence, the arrangement of the various components that are needed to complete an electrochemical cell can be done by using electrical circuit. This section considers some electrical circuit in some electrochemical instruments.

3.3 Polarization circuit

Fig. 7.2 shows the components needed for polarization study, using a potentiostat. It can be seen from the diagram that voltmeter, ammeter, electrodes (reference electrode, working electrode and counter electrodes) are needed.

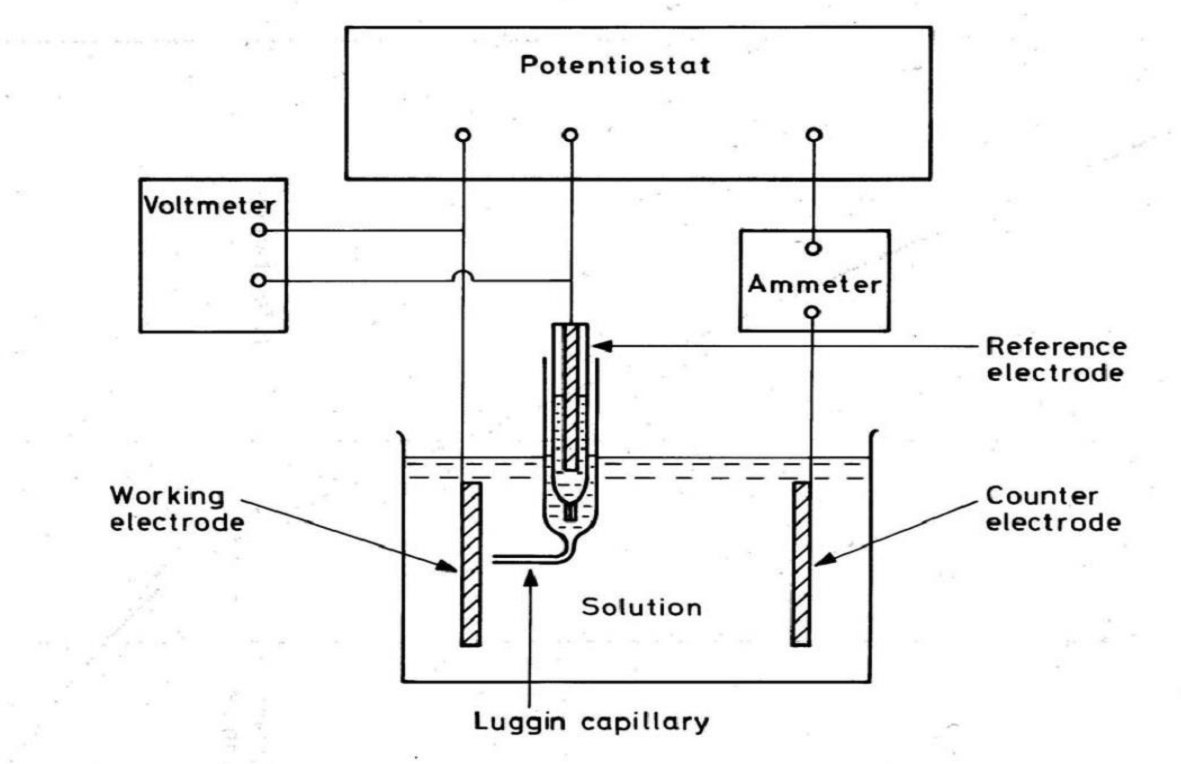


Fig. 7.2: Block diagram, showing components for polarization study using a potentiostat

In Fig. 7.3 the arrangement show in Fig. 7.2 is presented**.**

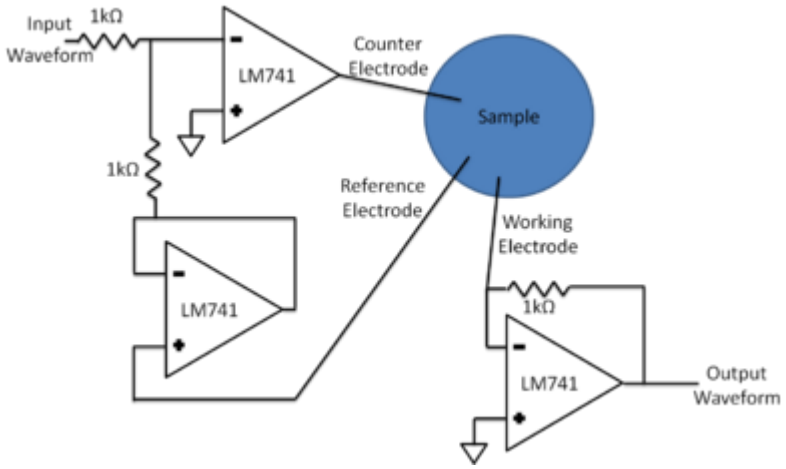


Fig. 7.3: Circuit diagram for potentiostat

(Source: http://2011.igem.org/Team:Calgary/Project/Reporter/Prototype)

3.4 Circuit for measuring emf

In Fig. 7.4, a circuit for measuring emf is presented. where E is the power source, E_S is the standard or known cell and E_X is the unknown cell. EMF is the potential when the cell is no producing any current. It is sometime called the zero current or open circuit potential. In order to measure the emf of a cell, the potentiometer slide wire is adjusted until there is no current through the galvanometer (G) When the slide is in position 2, then $R = R_S$. The process is repeated for position 1, where $R = R_X$. From the above, $E_X = I_0R_X$ and $E_S = I_0R_S$. At equilibrium, $E_X = E_S$ and $E_X = (R_X/R_S)E_S$.

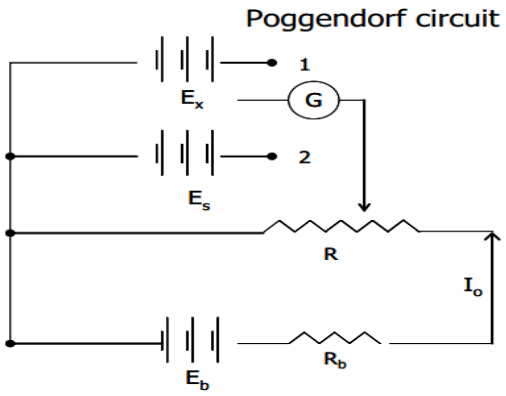


Fig. 7.4:Electric circuit for measuring emf or pzc of a cell

3.5 Electrochemical impedance spectroscopy

A Randles circuit is an equivalent electrical circuit that consists of an active electrolyte resistance R_S in series with the parallel combination of the double-layer capacitance C_{dl} and an impedance of a faradaic reaction. It is commonly used in electrochemical impedance spectroscopy (EIS) for interpretation of impedance spectra, often with a constant phase element (CPE) instead of the double layer capacity (C_{dl}).

Figure 48 shows the equivalent circuit initially proposed by John Edward BroughRandles for modelling of interfacial electrochemical reactions in presence of semi-infinite linear diffusion of electroactive particles to flat electrodes. In this model, the impedance of a faradaic reaction consists of an active charge transfer resistance R_{ct} and a specific electrochemical element of diffusion W, which is also called Warburg element ($Z_W = A_W/(j\omega)^{0.5}$, where A_W is Warburg coefficient, j – imaginary unit, ω – angular frequency).

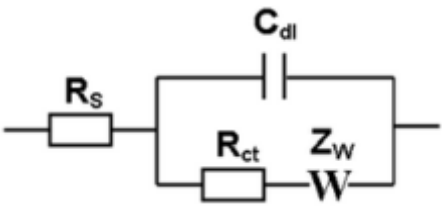


Fig. 7.5: Randles circuit schematic.

Worked example 28

(a) Draw a labelled diagram of a potentiostat circuit indicates the basic component of the circuit

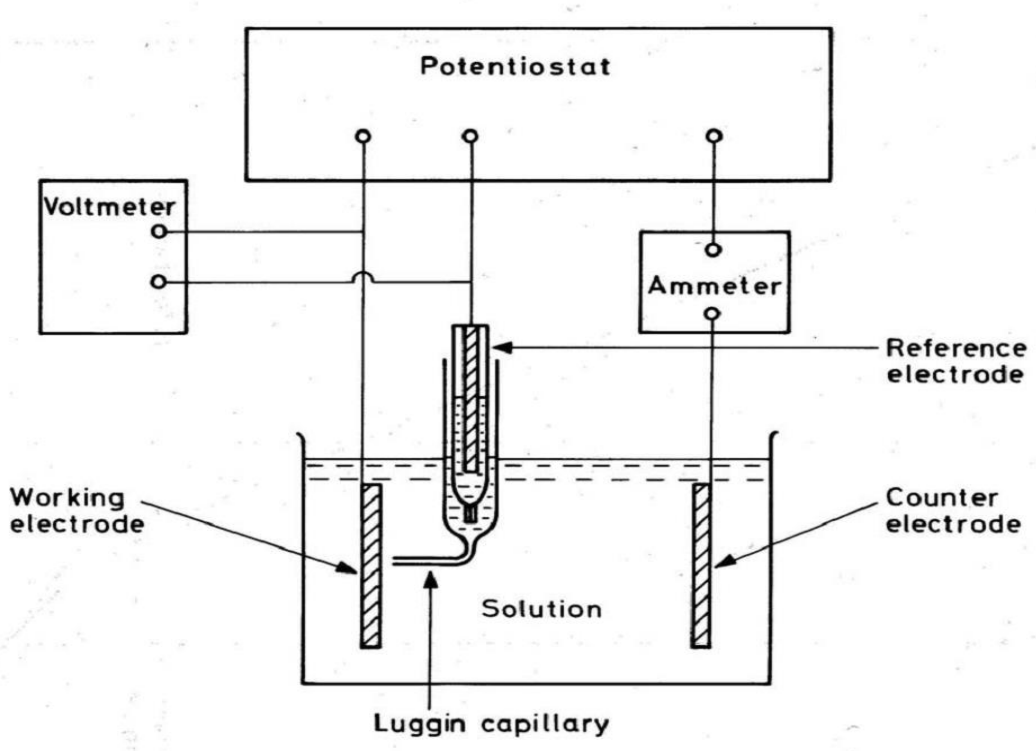
(b) What is emf

(b) Draw a labelled circuit diagram for measuring emf of a cell. Hence explain how the emf can be measured

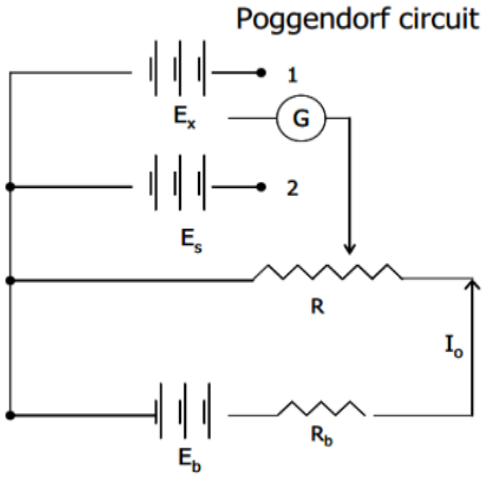
Solution

The major electrodes are working electrode, counter electrode and reference electrode

(b) EMF is the potential when the cell is no producing any current. It is sometime called the zero current or open circuit potential



(c) The diagram for measuring emf of a cell is given below



In order to measure the emf of a cell, the potentiometer slide wire is adjusted until there is no current through the galvanometer (G) When the slide is in position 2, then R = RS. The process is repeated for position 1, where R = RX. From the above, $E_X = I0R_X$ and $E_S = I0R_S$.At equilibrium, EX = ES and $E_X = (R_X/R_S)$

4.0 Self Assessment Exercises and Answers

1.(a) Most electrochemical instruments operate by measuring some physical process. Give four examples of such physical process

(b) (i) List five functional parts of an electrochemical instrument and use a flow sheet to explain how they are connected. (ii) Define the term, signal (iii) What is a transducer?

(iv) Why is the pH electrode said to be a transducer?

2. Define the term, sensitivity and selectivity of a transducer in an electrochemical instrument.

3. Draw a block diagram of a circuit that can be used for polarization study

4. Draw a labelled circuit that can be used to measure electromotive force of a cell or potential at zero charge.

5.(a) Given that the equation representing the reaction taking place in a pH meter is $H^+ + e^- = ½ H_2$. Derive an expression to show the relationship between potential and pH

(b) Given that the temperature of a solution whose voltage is to be measured at pH = 6, Calculate the measured voltage when E_0 = 0.06 mV

(c) What is the major factor that should be considered when choosing a signal processor?

Answer to Self Assessment Exercises

1(a) The physical processes are

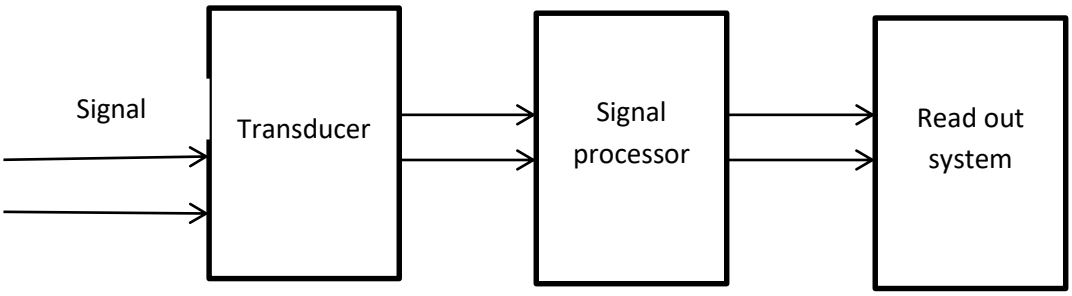
i. amount of current,

ii. voltage,

iii. resistant,

iv. capacitance, etc.

(b)(i) An electrochemical instrument will have a signal as the input, a transducer, signal processor and read out system as the functional elements as shown below



Input signal enters the instrument through the transducer. The transducer produces an internal signal which has to be amplified before it can be read from the read-out system.

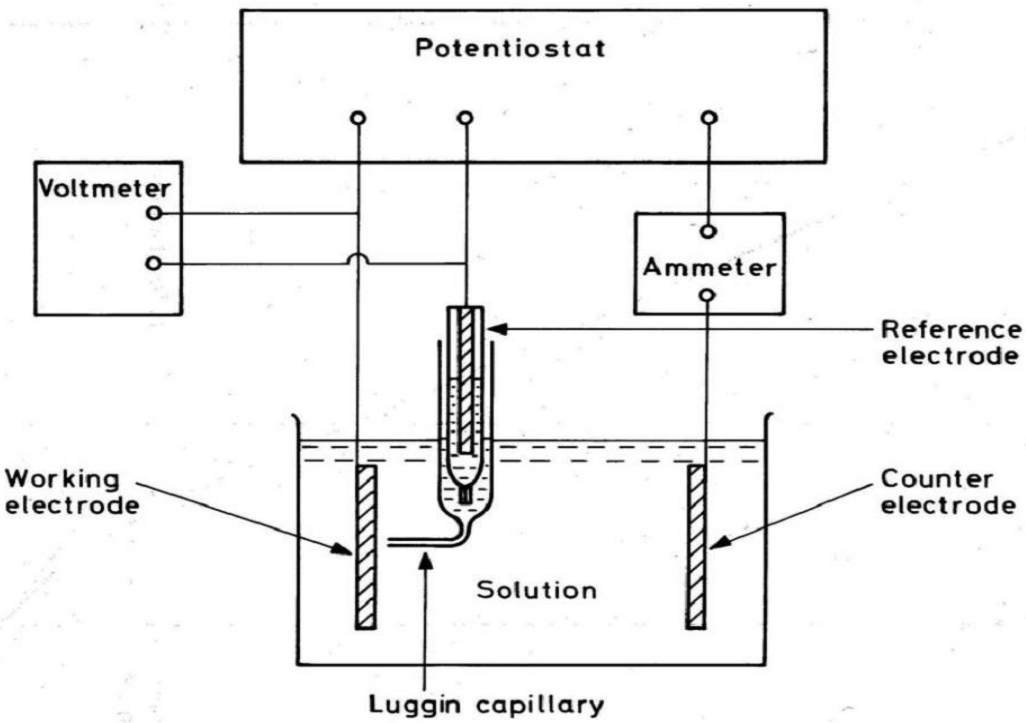
(ii) A signal represents some form of information or a means of carrying the information.

(iii) A transducer is a functional element of an instrument which receives the input signal and produces an output signal (internal signal) that has to pass through a signal processor. All transducers work through some form of physical properties.

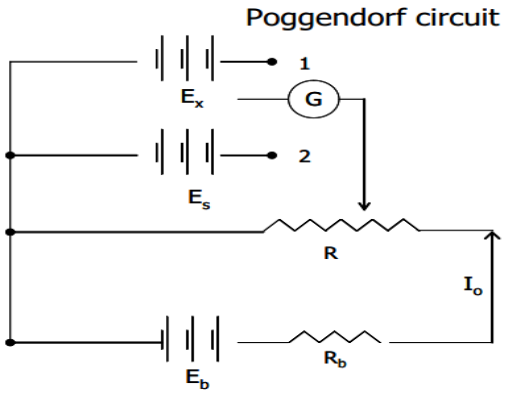
(iv) A transducer is used to convert energy or information (input signal) from one form to another. The pH electrode for example is a transducer that responds to a change in the potential difference between a liquid in a sealed glass and the sample solution to be measured

2. The sensitivity of a transducer is defined as the ratio of the magnitude of the output signal to the magnitude of the input signal. Its selectivity is also defined as the ratio of its sensitivity to the input signal (to be measured) to the sensitivity to other input signal.

3. The labelled diagram is shown below



4. A labelled circuit for measuring the electromotive force (emf) or potential at zero charge (pzc) of a cell is shown below



5(a) Theoretical voltage output from a pH meter can be calculated from the Nernst equation.

The chemical equation that is significant in pH study is

$$H^+ \quad + \quad e^- \quad = \quad \tfrac{1}{2} H_2$$

Applying the Nernst equation to the above reaction, we have,

$$E_H = E^0 - \frac{2.303RT}{F} log a^+_{H+}$$

$$E_H = E^0 - \frac{2.303RT}{F} pH$$

The above equation can be simplified to the following form

$$E_v - E_0 \quad = \quad -0.198T(pH - 7.0) \qquad\qquad 123$$

where E_V is the voltage being measured in millivolt and T is the temperature of the solution in Kelvin. The value of E_0 depends on the particular electrode being used and is almost constant for a given electrode.

(b) Given, T = 273 K, pH = 12, E_0 = 0.06 mV. Therefore,

$$E_v \quad = \quad -0.198T(pH - 7.0) + E_0$$

$$E_v \quad = \quad -0.198 \times 273\,K \times (6 - 7.0) + 0.06 = 54.14\,mV$$

(c) Generally, in all electrochemical instruments, the output signal determined the type of signal processor that is required.

(ii) Class Activity

Explain how you can assembly components to form an electrochemical cell for

(i) potentiodynamic measurement (ii) Electrochemical impedance spectroscopic measurement (20 minutes)

5.0 Conclusion

Electrochemical instrument are built from various functional components that interact to form the expected unit. Each unit must synchronize with each other and once they are under operation, they work as a system.

6.0 Summary

Electronics is the science of how to control the electrical energy, in which the electrons have a fundamental role. Electronics deals with electrical circuits that involve active electrical components such as vacuum tubes, transistors, diodes and integrated circuits, and associated passive electrical components and interconnection technologies. The essential components of electrochemical instruments are impedance, input/output devices, etc.

7.0 References/Further Readings

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APPENDIX: GENERAL TEST QUESTIONS

(1) What is an electric double layer

(2) Write an equation that relates flux to Fick's law and define all terms used

(3) List the three parameter\in which conductivity of an electrolyte relates proportionally

(4) Draw a block and labelled diagram (flow chart) of a measuring instrument and explain how signal is transmitted and read out

(5) State the three major electrochemical interface that you know and give the order of their relative strength.

(6) Highlight the two types of transport process that can be encountered in an electrolytic cell

(7) In an electrochemical cell, the anodic Tafel constant is 0.1 when the anodic current is 10V and the exchange current density is 1 V. Calculate the anodic polarization

(8) Highlight the principle behind the Guao Chapman theory of electric double layer

(9) What is the significance of Ilkovic equation in electrochemistry

(10) What are the factors that affects mobility of ions in solution

10. Briefly differentiate between galvanic and electrolytic cell. In what way are the two cells similar?

11. Consider the following cell reaction, $Zn_{(s)}/Zn^{2+}//Cu^{2+}{}_{(aq)}/Cu_{(s)}$ cell reaction.

    (i) Write equations for anodic and cathodic reactions in the cell

    (ii) Identify the cathode, anode and the cells where oxidation and reactions occur

    (iii) Write the overall cell reaction for the system

12. What are the common electrolytes that can be used in a construction of a salt bridge. What is the major function of a salt bridge in an electrochemical cell?

13. Highlight the different processes that can create a difference in potential in an electrochemical system

14. List the three major electrochemical interphases that you know and explain the order expected for diffusion of ions or other elementary particles in each of them

15. What are the factors that are responsible for a complex distribution of charge within the interphase region of an electrochemical system

16. In every electrochemical system, it is required that there should be an anode and a cathode. If a piece if iron metal is immersed in a solution of HCl, do you expect to have the anode and the cathode in that system. Give reason for your answer

17. What are the parameters that affects the structure of an electric double layer:

18. Given an electrochemical cell, identify the three major zones that exist between an electrode and electrolyte and explain why the concentration of ions in each of the zone is expected to differ.

19. Use the Nernst equation to described the dependence of the electrode potential of an electrochemical system on the concentrations of the oxidized and the reduces species.

20. State Fick's first law of diffusion. Given that C_A and C_B denote the concentration of diffusing specie at the bulk and surface respectively. Under what condition, can we obtain a mathematical equation that relates these concentrations with the limiting current (i_L)?

21. Write an expression that relates cathodic over potential to the cathodic current (i_C) and the limiting current (i_L). From the expression, state what will happened to the overpotential if (a) $i_c > i_L$ (b) $i_C < i_L$ (c) $i_C = i_L$

22. Write an expression for (a) total anodic polarization (b) total cathodic polarization (c) Sketch Evans diagram to show the expected graphs for the different polarization

23. Briefly highlight the contribution of Tafel and Butler-Volmer to the development of electrochemistry. In what way did Butler Volmer improve Tafel equation?

24. Differentiate between polarizable and non-polarizable electrode

25. In what ways can the cathode and the anode be polarised. Use suitable equation to explain your answer

26. What is the difference between over voltage arising from cathodic and anodic polarization respectively?

27. Briefly describe how you can estimate Tafel constant for anodic and cathodic polarization, given that exchange current density, anodic current and cathodic current are provided. Draw suitable diagram to support your explanation.

28. What is the difference between polarization of a single electrode and polarization of a two-electrode system?

29. What is the importance of mass transport in polarography?

30. Sketch a typical nature of a polarogram and explain important parameters that can be obtained from such plot

31. What is the significant of half wave potential in polarography?

32. What is the importance of diffusion current in polarography? Write the Ilkovic equation and explain how the diffusion current connects with measurable quantities. Finally, how can this equation be applied for analytical purpose?

33. Define the term, flux as it relates to mass transport in electrochemistry. In what way does the flux relates to Fick's first law of diffusion?

34. What are the three major aspect of mass transport in electrochemistry? Write a general equation to show how these three aspects are related to mass transport

35. What is the significant of Stokes' law in mass transport? Use suitable mathematical derivation to support your answer

36. Write the general form of the Levich equation. What is the significance of the equation in electrochemistry?

37.(a) What are the component of the Leclanche dry cell?

(b) Write the anodic and cathodic half reactions for the cell

(c) Also write the overall cell reaction for the cell

(d) The Leclanche dry cell is inexpensive to produce and is capable of producing up to 1.55 V. What are the factors that limits its efficiency?

38.(a) With the aid of appropriate equation, define the term, flux

(b) Define diffusion flux

(c) State the three-principal mechanism through which ions are transferred from solution to an electrode (in the absence of fluid turbulence)

(d) Write and equation to represent the rate of transfer of ion in the y-direction and relates each term in the equation to the three-principal mechanism, stated in c above

39. Write Onsager equation and compare the equation with Kohlrausch law

40. Derive an expression for activity coefficient of a 1:1 electrolyte

41. Calculate the ionic strength, mean ionic activity coefficient and mean ionic molarity of 0.04 M of $ZnCl_2$

42. (a)Conductivity of an electrolyte is proportional to some parameters. List the parameters and define the term, mobility

(b) Given that $F = eEz = \frac{ze\Delta\phi}{L}$. Derive an expression for the transport number of cation and anion